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PATENT ABSTRACTS OF JAPAN

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(71)Applicant : NISSAN MOTOR CO LTD

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(72)Inventor : YAMAMOTO SHINJI

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Priority number : 11336839

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Priority country : JP

(54) EXHAUST GAS CLEANING CATALYST

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an exhaust gas cleaning catalyst with which NOx can be cleaned with high efficiency by using H₂ as a reducing agent under an oxygen-excess atmosphere, an HC component and CO component to be not cleaned and discharged in a usual catalyst can be reduced and particularly the HC component can be remarkably reduced in a low temperature region just after an engine is started and which gives highly fuel-efficient effect.

SOLUTION: This catalyst is obtained by layering a zeolite-containing HC adsorbing layer on an integrated structure type carrier and layering a hydrogen generating and nitrogen oxides cleaning catalyst layer, where hydrogen is generated from hydrocarbon and/or carbon monoxide contained in the exhaust gas and nitrogen oxides are cleaned by using the generated hydrogen, on the HC adsorbing layer.

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(54) 【発明の名称】 排気ガス浄化用触媒

(57) 【要約】

【課題】 酸素過剰雰囲気下において、 H_2 を還元剤として NO_x を高効率で浄化し、且つ、未浄化で排出されていたHC、CO成分、特にエンジン始動後の低温域でのHCを著しく低減し、しかも燃費向上効果の高い排気ガス浄化用触媒を提供すること。

【解決手段】 一体構造型担体上にHC吸着層を積層し、この上に H_2 生成・ NO_x 浄化触媒層を積層して成る排気ガス浄化用触媒であって、HC吸着層がゼオライトを含有し、 H_2 生成・ NO_x 浄化触媒層が、炭化水素及び／又は一酸化炭素から水素を生成し、生成した水素を用いて窒素酸化物を浄化する。

【特許請求の範囲】

【請求項 1】 一体構造型担体上に H₂ 吸着層を積層し、この上に H₂ 生成・NO_x 浄化触媒層を積層して成る排気ガス浄化用触媒であって、上記 H₂ 生成・NO_x 浄化触媒層が、炭化水素及び／又は一酸化炭素から水素を生成し、生成した水素を用いて窒素酸化物を浄化することを特徴とする排気ガス浄化用触媒。

【請求項 2】 上記 H₂ 生成・NO_x 浄化触媒層が、対象とする内燃機関のコールド運転時に上記 H₂ 吸着層に吸着し暖機運転過程で脱離する炭化水素と、内燃機関の暖機運転後に排出される炭化水素及び／又は一酸化炭素から水素を生成し、これら水素と排気ガス中の炭化炭素及び／又は一酸化炭素を用いて窒素酸化物を浄化することを特徴とする請求項 1 記載の排気ガス浄化用触媒。

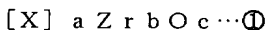
【請求項 3】 上記 H₂ 生成・NO_x 浄化触媒層が H₂ 生成触媒成分と NO_x 浄化触媒成分とを含み、上記 H₂ 生成触媒成分は、炭化水素を改質して水素を生成する H₂ 改質成分と、CO を水蒸気改質して水素を生成する CO 改質成分とを含有し、上記 H₂ 改質成分は、パラジウムを担持したセリウム酸化物を含有し、上記 CO 改質成分は、ロジウムを担持したジルコニウム酸化物を含有し、

上記 H₂ 生成・NO_x 浄化触媒層が、上記 H₂ 改質成分と上記 CO 改質成分とが混合されて同一層を形成すること、上記 H₂ 改質成分の上に上記 CO 改質成分が積層されること、又は排気ガスの流れ方向の上流側に上記 H₂ 改質成分が配置され且つ下流側に上記 CO 改質成分が配置されることのいずれかから構成されていることを特徴とする請求項 1 又は 2 記載の排気ガス浄化用触媒。

【請求項 4】 上記 H₂ 生成・NO_x 浄化触媒層の触媒入口側部分が、パラジウムを担持したアルミナを含有する触媒層を含むことを特徴とする請求項 1～3 のいずれか 1 つの項に記載の排気ガス浄化用触媒。

【請求項 5】 上記窒素酸化物を浄化するときの触媒入口の排気ガスが、水素量／全還元成分量 ≥ 0.3 で表されるガス組成を満足することを特徴とする請求項 1～4 のいずれか 1 つの項に記載の排気ガス浄化用触媒。

【請求項 6】 上記ロジウムを担持したジルコニウム酸化物が、アルカリ土類金属を含有し、その組成が次式①



(式中の X は、マグネシウム、カルシウム、ストロンチウム及びバリウムから成る群より選ばれた少なくとも 1 種の元素、a 及び b は、原子比率、c は、X 及び Z r の原子価を満足するのに必要な酸素原子数を示し、 $a = 0.01 \sim 0.5$ 、 $b = 0.5 \sim 0.99$ 、 $a + b = 1$ を満たす) で表されることを特徴とする請求項 3～5 のいずれか 1 つの項に記載の排気ガス浄化用触媒。

【請求項 7】 上記 H₂ 吸着層、上記 H₂ 改質成分を含有する触媒層、上記 CO 改質成分を含有する触媒層及び

上記パラジウムを担持したアルミナを含有する触媒層から成る群より選ばれた少なくとも 1 つの触媒層が、NO_x 浄化触媒成分を含有することを特徴とする請求項 4～6 のいずれか 1 つの項に記載の排気ガス浄化用触媒。

【請求項 8】 上記 H₂ 吸着層、上記 H₂ 改質成分を含有する触媒層、上記 CO 改質成分を含有する触媒層及び上記パラジウムを担持したアルミナを含有する触媒層から成る群より選ばれた少なくとも 1 つの触媒層が、パラジウム、白金、ロジウム、アルミナ、アルカリ金属及びアルカリ土類金属から成る群より選ばれた少なくとも 1 種の NO_x 還元成分を含有することを特徴とする請求項 4～7 のいずれか 1 つの項に記載の排気ガス浄化用触媒。

【請求項 9】 上記アルカリ金属及び／又はアルカリ土類金属が、カリウム、セシウム、マグネシウム、カルシウム及びバリウムから成る群より選ばれた少なくとも 1 種の元素を含有することを特徴とする請求項 8 記載の排気ガス浄化用触媒。

【請求項 10】 上記 H₂ 吸着層が、Si / 2Al 比 = 10～500 の H 型 β -ゼオライトを含有することを特徴とする請求項 1～9 のいずれか 1 つの項に記載の排気ガス浄化用触媒。

【請求項 11】 上記 H₂ 吸着層が、H 型 β -ゼオライトと、MFI、Y 型、USY 及びモルデナイトから成る群より選ばれた少なくとも 1 種のゼオライトとを含有することを特徴とする請求項 1～10 のいずれか 1 つの項に記載の排気ガス浄化用触媒。

【請求項 12】 上記 H₂ 吸着層のゼオライトが、パラジウム、マグネシウム、カルシウム、ストロンチウム、バリウム、銀、イットリウム、ランタン、セリウム、ネオジム、リン、ホウ素及びジルコニウムから成る群より選ばれた少なくとも 1 種の元素を含有することを特徴とする請求項 10 又は 11 記載の排気ガス浄化用触媒。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、排ガス浄化用触媒に係り、更に詳細には、酸素過剰排ガス中の窒素酸化物 (NO_x) を高効率で浄化する排気ガス浄化用触媒に関する。

【0002】

【従来の技術】 従来、自動車等の内燃機関の排気ガス浄化用触媒として、一酸化炭素 (CO) 及び炭化水素 (HC) の酸化と NO_x の還元とを同時に行う触媒が汎用されている。このような触媒としては、耐火性担体上のアルミナコート層に、パラジウム (Pd)、白金 (Pt) やロジウム (Rh) 等の貴金属を担持させたもの及び必要に応じて助触媒成分としてセリウム (Ce)、ランタン (La) 等の希土類金属やニッケル (Ni) 等のペースメタル酸化物を添加したもの等が開示されている (特開昭 58-20307 号公報)。上記公報に開示されて

いる触媒は、排ガス温度及びエンジンの設定空燃比の影響を強く受け、特に内燃機関の排ガスが酸素過剰のときには、 NO_x を浄化することができない。このような内燃機関の排ガスが酸素過剰の時に窒素酸化物を浄化する方法として、特許掲載2600429号公報に、排ガスが酸素過剰のときに NO_x を吸蔵させ、その後酸素濃度を低下させて一時的にリッチ雰囲気にするにより、吸蔵された NO_x を放出して浄化処理する、いわゆるリッチスパイクによる方法が開示されている。

【0003】

【発明が解決しようとする課題】しかしながら、上記公報で開示されているような、リッチスパイクによる方法では、酸素過剰の運転領域においても定期的に排ガス中の酸素濃度を低下させる必要があり、更に、酸素濃度が低下した条件下で NO_x を還元反応させるために、還元剤として多量の HC 、 CO を供給する必要があり、酸素過剰で走行することによる燃費向上の効果が十分に得られないという課題があった。

【0004】更に、酸素過剰雰囲気において NO_x を吸蔵させるために多量のアルカリ金属元素やアルカリ土類金属元素を含有させるが、このために活性金属である Pt 、 Pd 及び Rh の低温時の酸化活性が十分に得られなくなる。また、 NO_x 浄化反応で消費されなかった HC 、 CO 成分を十分に浄化するためには、酸化反応で浄化させるか、 NO_x 浄化触媒の後段に三元触媒を配置して浄化する必要がある。しかしながら、このような触媒システムでは、 HC 、 CO を浄化する触媒が排気流路の後段に配置されるため、十分な HC 、 CO の浄化性能が得られず、特にエンジン始動直後に排出される HC 、 CO 成分浄化が困難であるという課題もあった。

【0005】本発明は、このような従来技術の有する課題に鑑みてなされたものであり、その目的とするところは、酸素過剰雰囲気下において、 NO_x を高効率で浄化し、且つ、未浄化で排出されていた HC 、 CO 成分、特にエンジン始動後の低温域での HC を著しく低減し、しかも燃費向上効果の高い排気ガス浄化用触媒を提供することにある。

【0006】

【課題を解決するための手段】本発明者は、上記課題を解決すべく、鋭意検討を行った結果、特定の HC 改質処理と CO 水蒸気改質処理等を行って H_2 を生成し、この H_2 を NO_x 還元剤とすることにより、上記課題が解決できることを見出し、本発明を完成するに至った。

【0007】即ち、本発明の排気ガス浄化用触媒は、一体構造型担体上に HC 吸着層を積層し、この上に H_2 生成・ NO_x 浄化触媒層を積層して成る排気ガス浄化用触媒であって、上記 H_2 生成・ NO_x 浄化触媒層が、炭化水素及び／又は一酸化炭素から水素を生成し、生成した水素を用いて窒素酸化物を浄化することを特徴とする。

【0008】また、本発明の排気ガス浄化用触媒の好適

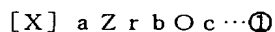
形態は、上記 H_2 生成・ NO_x 浄化触媒層が、対象とする内燃機関のコールド運転時に上記 HC 吸着層に吸着し暖機運転過程で脱離する炭化水素と、内燃機関の暖機運転後に排出される炭化水素及び／又は一酸化炭素から水素を生成し、これら水素と排気ガス中の炭化炭素及び／又は一酸化炭素を用いて窒素酸化物を浄化することを特徴とする。

【0009】更に、本発明の排気ガス浄化用触媒の他の好適形態は、上記 H_2 生成・ NO_x 浄化触媒層が H_2 生成触媒成分と NO_x 浄化触媒成分とを含み、上記 H_2 生成触媒成分は、炭化水素を改質して水素を生成する HC 改質成分と、 CO を水蒸気改質して水素を生成する CO 改質成分とを含有し、上記 HC 改質成分は、パラジウムを担持したセリウム酸化物を含有し、上記 CO 改質成分は、ロジウムを担持したジルコニウム酸化物を含有し、上記 H_2 生成・ NO_x 浄化触媒層が、上記 HC 改質成分と上記 CO 改質成分とが混合されて同一層を形成すること、上記 HC 改質成分の上に上記 CO 改質成分が積層されること、又は排気ガスの流れ方向の上流側に上記 HC 改質成分が配置され且つ下流側に上記 CO 改質成分が配置されることのいずれかから構成されていることを特徴とする。

【0010】更にまた、本発明の排気ガス浄化用触媒の他の好適形態は、上記 H_2 生成・ NO_x 浄化触媒層の触媒入口側部分が、パラジウムを担持したアルミナを含有する触媒層を含むことを特徴とする。

【0011】また、本発明の排気ガス浄化用触媒の更に他の好適形態は、上記窒素酸化物を浄化するときの触媒入口の排気ガスが、水素量／全還元成分量 ≥ 0.3 で表されるガス組成を満足することを特徴とする。

【0012】更にまた、本発明の排気ガス浄化用触媒の他の好適形態は、上記ロジウムを担持したジルコニウム酸化物が、アルカリ土類金属を含有し、その組成が次式①



(式中の X は、マグネシウム、カルシウム、ストロンチウム及びバリウムから成る群より選ばれた少なくとも1種の元素、 a 及び b は、原子比率、 c は、 X 及び Zr の原子価を満足するのに必要な酸素原子数を示し、 $a = 0.01 \sim 0.5$ 、 $b = 0.5 \sim 0.99$ 、 $a + b = 1$ を満たす)で表されることを特徴とする。

【0013】また、本発明の排気ガス浄化用触媒の他の好適形態は、上記 HC 吸着層、上記 HC 改質成分を含有する触媒層、上記 CO 改質成分を含有する触媒層及び上記パラジウムを担持したアルミナを含有する触媒層から成る群より選ばれた少なくとも1つの触媒層が、 NO_x 浄化触媒成分を含有することを特徴とする。

【0014】更にまた、本発明の排気ガス浄化用触媒の他の好適形態は、上記 HC 吸着層、上記 HC 改質成分を含有する触媒層、上記 CO 改質成分を含有する触媒層及

び上記パラジウムを担持したアルミナを含有する触媒層から成る群より選ばれた少なくとも1つの触媒層が、パラジウム、白金、ロジウム、アルミナ、アルカリ金属及びアルカリ土類金属から成る群より選ばれた少なくとも1種のNO_x還元成分を含有することを特徴とする。

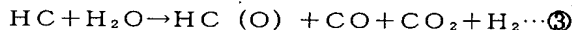
【0015】また、本発明の排気ガス浄化用触媒の更に他の好適形態は、上記HC吸着層が、Si/2Al比=10～500のH型β-ゼオライトを含有することを特徴とする。

【0016】更にまた、本発明の排気ガス浄化用触媒の他の好適形態は、上記HC吸着層が、H型β-ゼオライトと、MFI、Y型、USY及びモルデナイトから成る群より選ばれた少なくとも1種のゼオライトとを含有することを特徴とする。

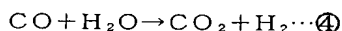
【0017】また、本発明の排気ガス浄化用触媒の他の好適形態は、上記HC吸着層のゼオライトが、パラジウム、マグネシウム、カルシウム、ストロンチウム、バリウム、銀、イットリウム、ランタン、セリウム、ネオジム、リン、ホウ素及びジルコニウムから成る群より選ばれた少なくとも1種の元素を含有することを特徴とする。

【0018】

【発明の実施の形態】以下、本発明の排気ガス浄化用触媒について詳細に説明する。なお、「%」は特記しない*

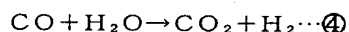
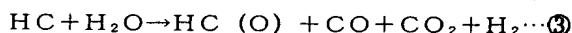
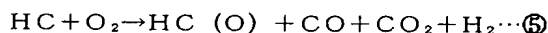


(式中のHC(O)は改質反応後のHCを示す)で表され、また上記CO水蒸気改質反応は、次式④

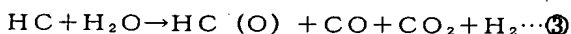
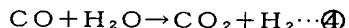


で表されることが考えられている。

【0021】上記HC・CO改質反応によりH₂を生成させるに際し、上記H₂生成・NO_x浄化触媒層は、上記HC吸着層上に積層される。この層は、HCを改質してH₂を生成するHC改質成分とCOを水蒸気改質してH₂を生成するCO改質成分とが混合されて一つの層を形成し、又はHC改質成分を含むHC改質成分層と、CO改質成分を含むCO水蒸気改質層とが積層されている多層を形成するが、特に、HC改質成分層の上にCO水蒸気改質成分層を積層した構造を採ることが好ましい。図1に示したように、エンジン始動直後に上記HC吸着層に吸着され、触媒暖機過程で上記HC吸着層から放出されたHCは、まず、上記HC改質成分層で部分酸化物、HC(O)、CO及びH₂に改質され、更に上記CO水蒸気改質成分層でCOがH₂に変成される。このよ※



の反応が起こり、上記CO水蒸気改質成分層において★★は、主に次式③、④及び⑥



*限り、質量百分率を示す。本発明の排気ガス浄化用触媒は、一体構造型担体上に、HC吸着層を積層し、この上に、H₂生成・NO_x浄化触媒層を積層して成る。

【0019】上記HC吸着層は、コールドHC吸着能を持つゼオライトを主成分とし、対象とする内燃機関のコールド運転時、即ちエンジン始動直後で触媒がまだ低温であるときにはHCを吸着し、触媒暖機過程(150～300℃)にあるときにはHCを脱離する。次に、上記HC吸着層に積層されているH₂生成・NO_x浄化触媒層は、後述するHC・CO改質反応により、脱離HCからH₂を生成し、更に、内燃機関の定常運転時に排出されるHC及び/又はCOからもH₂を生成することができる。これらの生成されたH₂は、NO_x還元剤として排ガス中のNO_xとよく反応する。このとき、H₂生成・NO_x浄化触媒層に含まれるNO_x浄化触媒成分は、温度が上昇しておらず十分に活性化してはいないが、H₂とNO_xとの反応性が高いため、エンジン始動直後から酸素過剰雰囲気気の運転制御に到達するまでの触媒暖機過程に排出されるNO_xを効率よく浄化することができる。と推察される。

【0020】また、上記H₂生成・NO_x浄化触媒層で行われる上記HC・CO改質反応は、一般的には、HCの改質反応とCO水蒸気改質反応に分けることができ、このHC改質反応は、次式②及び③

※うな構造を採ることにより、上述の如く触媒暖機過程においても、排気ガス中に含まれるHC及びCOを改質しH₂を生成できるので、酸素過剰運転領域においても、H₂を供給し、触媒暖機後もNO_xを浄化処理できる。なお、HCがHC改質反応、CO水蒸気改質反応の順で変成されればよいので、上記HC改質成分層と上記CO水蒸気改質成分層が排気ガス流路に沿ってタンデム配置を採ってもよく、上記多層構造に特に限定されるものではない。

【0022】

更に、HCを改質しH₂を生成するためには、上記HC改質成分層にPdを担持したセリウム酸化物を含有させることが好ましく、COを水蒸気改質してH₂を生成するためには、上記CO水蒸気改質成分層にRhを担持したジルコニウム酸化物を含有させることが好ましい。これらの貴金属や酸化物を含有させることにより、排ガスを本発明の排気ガス浄化用触媒内に通過させた場合、上記HC改質成分層においては、主に次式③～⑤



の反応が起こり、 H_2 が生成されるとともに排ガス成分、特にHCとCOが浄化される。

【0023】更にまた、上記 H_2 生成・ NO_x 浄化触媒層が上述のような H_2 生成触媒成分だけではなく、 NO_x 浄化触媒成分をも含むことにより、1つの触媒で NO_x 還元剤である H_2 を生成するとともに、 NO_x を効率よく浄化することができる。

【0024】更に、エンジン暖機過程終了後においても、排ガス中のHC、COから H_2 を有意に生成させるために、本発明の排気ガス浄化用触媒は、上流側の上記 H_2 生成触媒の一部、即ち該触媒入口側部分が、Pdを担持したアルミナを含有する触媒層を含むことが好ましい。例えば、本発明の排気ガス浄化用触媒の好適な一形態として、触媒入口側には上記HC吸着触媒層の上にPd担持アルミナを含有するHC部分酸化触媒が積層されており、その下流側には上記HC吸着層の上にPd担持セリウム酸化物を含有するHC改質成分層とRh担持ジルコニウム酸化物を含有するCO水蒸気改質成分層とが積層されている構造が挙げられる。図2に、上記構造を示すが、本発明の排気ガス浄化用触媒は特にこれに限定されるものではない。

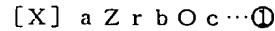
【0025】また、図2に示したように、触媒暖機後においては、上記該触媒入口側部分に配置したPdを担持したアルミナを含有する触媒層で、部分酸化反応により排気ガス中に含まれるHCが $\text{HC}(\text{O}) \cdot \text{CO}$ に変成され、次に、上記HC改質成分層で $\text{HC}(\text{O})$ の改質反応により H_2 生成が促進され、次いで上記CO水蒸気改質成分層で水蒸気改質反応によりCOと H_2O から CO_2 と H_2 が生成されていると推察される。従って、本発明においては、上述の触媒暖機過程に引き続いて、触媒暖機後も H_2 を供給でき、酸素過剰雰囲気下であっても NO_x を還元浄化できると考えられる。

【0026】このように、本発明の排気ガス浄化用触媒においては、 NO_x 浄化に用いる還元成分として、従来から主として用いられていたHC及びCOの代わりに又はこれに加えて H_2 を用いることができるが、更に、 NO_x 浄化するときの触媒入口の排気ガスは、 H_2 量/全還元成分量 ≥ 0.3 で表されるガス組成を満足することが好ましい。かかるガス組成を満足すれば、排気ガス中の H_2 濃度が高くなるので、更に高い NO_x 浄化性能を得ることができる。

【0027】即ち、従来、自動車エンジンからの排気ガスや排気ガス触媒を用いた場合の排気ガス中の H_2 比率は H_2 量/全還元成分量 < 0.3 であり、 H_2 の比率が低く、 H_2 を還元成分として有効利用することが不可能であったが、本発明ではこの比率を増大し、 H_2 を有効利用しているのである。なお、上記排気ガス組成は、 H_2 量/全還元成分量 ≥ 0.3 を満足すれば十分であるが、 H_2 量/全還元成分量 ≥ 0.5 とすることが更に好まし

い。

【0028】また、上記CO水蒸気改質成分層において、上記Rhの酸化状態をCO水蒸気改質反応に適した状態に維持するために、上記Rh担持ジルコニウム酸化物がアルカリ土類金属を含有して成ることが好ましく、その組成は、次式①



で表される。上記式①のXは、Mg、Ca、Sr又はBa及びこれらの任意の組み合わせに係る元素を示し、aは、該元素の原子比率、bは、Zrの原子比率、cは、該元素及びZrの原子価を満足するのに必要な酸素原子数を示し、また、 $a = 0.01 \sim 0.5$ 、 $b = 0.5 \sim 0.99$ 、 $a + b = 1$ を満たす。上記アルカリ土類金属を含有させれば、初期から耐久後まで高い触媒活性を得ることができる。

【0029】更に、上記HC吸着層、上記 H_2 生成・ NO_x 浄化触媒層又は上記Pdを担持したアルミナを含有する触媒層及びこれらの任意の組み合わせに係る触媒層は、 NO_x 浄化触媒成分を含有することが好ましい。即ち、上記HC吸着層、HC改質成分層、CO水蒸気改質成分層及び該触媒入口側部分に配置されたPdを担持したアルミナを含有する触媒層のいずれにも NO_x 浄化触媒成分であるPd、PtやRh等を含有させることができる。 NO_x 浄化触媒成分を含有させることによって、触媒暖機過程で H_2 を生成させると同時に、触媒暖機過程で排出される NO_x を効率よく浄化することができ、更には、触媒暖機後も酸素過剰雰囲気下での運転制御時に排出される NO_x を効率よく浄化することができる。なお、上述のように各触媒層に NO_x 浄化触媒成分を含有させるだけでなく、上記 H_2 生成・ NO_x 浄化触媒層の上に更に NO_x 浄化触媒層を積層してもよいし、各触媒層に NO_x 浄化触媒成分を含有させずに NO_x 浄化触媒層を積層してもよい。更には、排ガス流路上流側に本発明の排気ガス浄化用触媒を、下流側に NO_x 浄化用触媒をタンデム配置してもかまわない。

【0030】また特に、上記HC吸着層、HC改質成分層、CO水蒸気改質成分層又は上記触媒入口側部分に配置されているPdを担持したアルミナを含有する触媒層及びこれらの任意の組み合わせに係る触媒層は、Pd、Pt、Rh、アルミナ、アルカリ金属又はアルカリ土類金属及びこれらの任意の組み合わせに係る NO_x 浄化触媒成分を含有することができる。これらの NO_x 浄化成分を含有することによって、エンジン始動直後から酸素過剰雰囲気下の定常運転制御時まで、エンジンから排出される NO_x を効率よく浄化できる。なお、上記アルカリ金属及び/又はアルカリ土類金属としては、カリウム(K)、セシウム(Cs)、マグネシウム(Mg)、カルシウム(Ca)又はバリウム(Ba)及びこれらの任意の組み合わせに係る金属を挙げることができるが、これ

らに限定されるものではない。

【0031】更に、上記各触媒層全体における上記アルカリ金属及びアルカリ土類金属含有量が、本発明の排ガス浄化用触媒における該金属含有総量の80重量%以上になると、コールドリーン域において排出される NO_x を吸収できるが、80重量%未満になると、十分な NO_x 吸収能が得られない。また、上記各触媒層全体がアルカリ金属及びアルカリ土類金属の総量の80重量%以上を含有するためには、アルカリ金属及び／又はアルカリ土類金属が、不溶性の化合物及び／又は難溶性の化合物

【0032】また、上記HC吸着層で使用するゼオライトは、公知のゼオライトの中から適宜選択して使用することができるが、特に、常温から比較的高い温度で、しかも、水存在雰囲気下であっても十分なHC吸着能を有し、且つ、高い耐久性を有するものを選択することが好ましい。このようなゼオライトとしては、代表的に、 $\text{Si}/2\text{Al}$ 比が10～500のH型 β -ゼオライトが挙げられるが、特にこれに限定されるものではない。 $\text{Si}/2\text{Al}$ 比が10未満のゼオライトでは、排ガス中に共存する水分の吸着阻害が大きいため、有効にHCを吸着することができず、 $\text{Si}/2\text{Al}$ 比が500を超えるゼオライトでは、HC吸着能が低下してしまうことがある。

【0033】更に、エンジンから排出される排ガス成分に合わせて、細孔径や細孔構造の異なるMF I、Y型、USY又はモルデナイト及びこれらの任意の組み合わせに係るゼオライトを選択して、上記H型 β -ゼオライトに混合して用いれば、排ガス中のHCを効率よく吸着することができる。

【0034】なお、上記H型 β -ゼオライトでも十分なHC吸着能を有するが、上記各種ゼオライトに、Pd、Mg、Ca、ストロンチウム(Sr)、Ba、銀(Ag)、イットリウム(Y)、La、Ce、ネオジム(Nd)、リン(P)、ホウ素(B)又はジルコニウム(Zr)及びこれらの任意の組み合わせに係る元素を、イオン交換法、含浸法及び浸漬法等の通常の方法を用いて担持することにより、HC吸着性能やHC脱離抑制能を更に向上することができる。

【0035】また、本発明の排気ガス浄化用触媒の上記一体構造型触媒担体には、例えばハニカム担体があり、ハニカム材料としては、一般にセラミック等のコーゼライト質のものが多く用いられる。しかし、これに限られず、フェライト系ステンレス等の金属材料から成るハニカム材料を用いてもよく、更には触媒成分粉末そのものをハニカム形状に成形してもよい。

【0036】

【実施例】以下、本発明を実施例及び比較例により更に詳細に説明するが、本発明はこれら実施例に限定されるものではない。

【0037】[HC改質成分層の触媒粉末の調製] 硝酸Pd水溶液をセリウム酸化物(CeO_2)粉末に含浸し、乾燥・焼成してPd担持セリウム酸化物粉末Aを得た。この粉末のPd担持濃度は10%であった。また、 CeO_2 の代わりに、 $\text{ZrO}_2\cdot\text{CeO}_2$ とした以外は、粉末Aと同様の操作を繰り返して得た粉末を、粉末Bとし、 $\text{ZrO}_2\cdot\text{CeO}_2$ としたものを粉末C、 $\text{ZrO}_2\cdot\text{CeO}_2$ としたものを粉末D、 $\text{ZrO}_2\cdot\text{CeO}_2$ としたものを粉末Eとした。更に、Pd担持濃度を5%とした以外は、粉末Aと同様の操作を繰り返して得た粉末を粉末Fとした。

【0038】[CO水蒸気改質成分層の触媒粉末の調製] 硝酸Rh水溶液を $\text{CaO}_2\cdot\text{ZrO}_2$ 粉末に含浸し、乾燥・焼成してRh担持ジルコニウム酸化物粉末Gを得た。この粉末のRh担持濃度は6%であった。また、 $\text{CaO}_2\cdot\text{ZrO}_2$ の代わりに、 $\text{MgO}_2\cdot\text{ZrO}_2$ とした以外は、粉末Gと同様の操作を繰り返して得た粉末を粉末Hとし、 $\text{BaO}_2\cdot\text{ZrO}_2$ としたものを粉末I、 $\text{SrO}_2\cdot\text{ZrO}_2$ としたものを粉末J、 $\text{CaO}_2\cdot\text{MgO}_2$ としたものを粉末K、 $\text{CaO}_2\cdot\text{BaO}_2\cdot\text{MgO}_2\cdot\text{ZrO}_2$ としたものを粉末L、 $\text{CaO}_2\cdot\text{ZrO}_2$ としたものを粉末M、 $\text{CaO}_2\cdot\text{ZrO}_2$ としたものを粉末Nとした。

【0039】[Pdを担持したアルミナを含有する触媒層の触媒粉末の調製] 硝酸Pd水溶液を活性アルミナ(Al_2O_3)粉末に含浸し、乾燥・焼成してPd担持アルミナ粉末Oを得た。この粉末のPd担持濃度は15%であった。また、 Al_2O_3 の代わりに、Ceを3%含有する Al_2O_3 とした以外は、粉末Oと同様の操作を繰り返して得た粉末を粉末Pとし、Zrを3%含有する Al_2O_3 としたものを粉末Q、Laを3%含有する Al_2O_3 としたものを粉末R、Zrを10%含有する Al_2O_3 としたものを粉末Sとした。

【0040】[NO_x 浄化触媒成分を含有する触媒粉末の調製] 硝酸Pd水溶液を、 Al_2O_3 粉末に含浸し、乾燥・焼成してPd担持アルミナ粉末Tを得た。この粉末TのPd担持濃度は8%であった。ジニトロジアンミンPt酸水溶液を、 Al_2O_3 粉末に含浸し、乾燥・焼成してPt担持アルミナ粉末Uを得た。この粉末UのPt担持濃度は6%であった。硝酸Rh水溶液を、 Al_2O_3 粉末に含浸し、乾燥・焼成してRh担持アルミナ粉末Vを得た。この粉末VのRh担持濃度は4%であった。

【0041】[触媒調製1] β -ゼオライト($\text{Si}/2\text{Al}=25$) 900gとシリカゾル100gと純水1000gを混合粉碎してスラリーとし、コーゼライト質モノリス担体(900セル/4ミル、1.3L)に付着させ、乾燥・焼成したのち、ゼオライトコート量100

g/Lのゼオライト触媒を得た。次いで、粉末A706gと硝酸性アルミナバインダー12gと純水800gとを混合粉碎してスラリーとし、ゼオライト触媒に付着させ、乾燥・焼成し、ゼオライト触媒に72g/Lをコートした触媒Aを得た。この触媒AのPd担持量は、7.06g/Lであった。更に、粉末G588gと硝酸性アルミナバインダー12gと純水600gとを混合粉碎してスラリーとし、触媒Aに付着させ、乾燥・焼成し、触媒Aに60g/Lをコートした触媒AG1を得た。この触媒AG1のRh担持量は、3.53g/Lであった。触媒AG1は、図3に示す三層構造とした。また、β-ゼオライト(Si/2Al=25)の代わりに表2に示したHC吸着材を用いて、同様の操作を繰り返し、触媒AG2~7を得た。

【0042】[触媒調製2] 粉末B706gと硝酸性アルミナバインダー14gと純水800gを混合粉碎してスラリーとし、触媒調整1と同様の操作を繰り返して調製したゼオライト触媒に付着させ、乾燥・焼成し、ゼオライト触媒に72g/Lをコートした触媒Bを得た。この触媒BのPd担持量は、7.06g/Lであった。次に、粉末G588gと硝酸性アルミナバインダー12gと純水600gを混合粉碎してスラリーとし、触媒Bに付着させ、乾燥・焼成し、触媒Bに60g/Lをコートした触媒BGを得た。この触媒BGのRh担持量は、3.53g/Lであった。触媒BGは、図3に示す三層構造とした。また、粉末Bの代わりに粉末C~Fを用いて、同様の操作を繰り返して、触媒CG、DG、EG、FGを得た。

【0043】[触媒調製3] β-ゼオライト(Si/2Al=25)の代わりに表2に示したHC吸着材とした以外は、触媒調整1と同様の操作を繰り返し、ゼオライト触媒を得た。次に、粉末B706gと粉末A706gと硝酸性アルミナバインダー28gと純水1500gを混合粉碎してスラリーとし、ゼオライト触媒に付着させ、乾燥・焼成し、ゼオライト触媒に144g/Lをコートした触媒BAを得た。この触媒BAのPd担持量は、14.12g/Lであった。更に、粉末H588gと硝酸性アルミナバインダー12gと純水600gとを混合粉碎してスラリーとし、触媒BAに付着させ、乾燥・焼成し、触媒BAに60g/Lをコートした触媒BAHを得た。この触媒BAHのRh担持量は、3.53g/Lであった。触媒BAHは、図3に示す三層構造とした。また、粉末Hの代わりに粉末I~Nを用いて、同様の操作を繰り返して、触媒BAI、BAJ、BAK、BAL、BAM、BANを得た。

【0044】[触媒調製4] β-ゼオライト(Si/2Al=25)900gとシリカゾル100gと純水1000gを混合粉碎してスラリーとし、コーゼライト質モノリス担体(900セル/4ミル、1.3L)に付着させ、乾燥・焼成したのち、ゼオライトコート量50g

/Lのゼオライト触媒を得た。これに、粉末O471gと硝酸性アルミナバインダー9gと純水500gとを混合粉碎してスラリーとし、ゼオライト触媒の排気ガス入口側の1/4部分に付着させ、乾燥・焼成し、ゼオライト触媒に48g/Lをコートした触媒O1を得た。この触媒O1のPd担持量は、7.06g/Lであった。次いで、粉末B706gと粉末A706gと硝酸性アルミナバインダー28gと純水1000gとを混合粉碎してスラリーとし、触媒O1をコートしていない3/4部分に付着させ、乾燥・焼成し、144g/Lをコートした触媒OBAを得た。この触媒OBAの総Pd担持量は、21.18g/Lであった。更に、粉末L588gと硝酸性アルミナバインダー12gと純水600gとを混合粉碎してスラリーとし、触媒O1をコートしていない3/4部分に付着させ、乾燥・焼成し、触媒OBAに60g/Lをコートした触媒OBALを得た。この触媒OBALのRh担持量は、3.53g/Lであった。触媒OBALは、図4に示す構造とした。また、β-ゼオライト(Si/2Al=25)の代わりに表2に示すHC吸着材を用いてゼオライトコート量50g/Lのゼオライト触媒を作成し、粉末Oの代わりに粉末P~Sを、粉末Aの代わりに粉末B~Fを、粉末Lの代わりに粉末G~Kを用いて、同様の操作を繰り返して、触媒PBBK、QBCJ、RBDI、SBEH、OBFGを得た。

【0045】[触媒調製5] 粉末B706gと硝酸性アルミナバインダー14gと純水1000gとを混合粉碎してスラリーとし、触媒調製4と同様の操作を繰り返して得たゼオライト触媒に付着させ、乾燥・焼成し、72g/Lをコートした触媒B2を得た。この触媒B2のPd担持量は、7.06g/Lであった。次いで、粉末G588gと硝酸性アルミナバインダー12gと純水600gとを混合粉碎してスラリーとし、触媒B2に付着させ、乾燥・焼成し、触媒B2に60g/Lをコートした触媒BGを得た。この触媒BGのRh担持量は、3.53g/Lであった。更に、粉末T618gと、粉末U530gと、粉末V88gと、水酸化ナトリウムをNa₂O換算で20gと、酢酸バリウムをBaO換算で20gと、硝酸性アルミナバインダー14gと、純水1500gとを混合粉碎してスラリーとし、触媒BGに付着させ、乾燥・焼成し、触媒BGに147g/Lをコートした触媒BGN1を得た。この触媒BGN1のPd担持量は12.0g/L、Pt担持量は3.18g/L、Rh担持量は、3.88g/Lであった。触媒BGN1は、図5に示す構造とした。

【0046】[NO_x浄化用触媒の調製] 粉末T618gと、粉末U530gと、粉末V88gと、水酸化ナトリウムをNa₂O換算で20gと、酢酸バリウムをBaO換算で20gと、硝酸性アルミナバインダー14gと、純水1500gとを混合粉碎してスラリーとし、コーゼライト質モノリス担体(400セル/6ミル、

1. 3 L) に付着させ、乾燥・焼成し、147 g/L をコートした触媒 N1 を得た。この触媒 N1 の Pd 担持量は 4.94 g/L、Pt 担持量は 3.18 g/L、Rh 担持量は、0.35 g/L であった。触媒 N1 は、単層構造とした。また、水酸化ナトリウムの代わりに酢酸マグネシウムを用い、同様の操作を繰り返して、MgO として 10 g/L、BaO として 10 g/L を担持した触媒を触媒 N2 を得た。

【0047】〔三元触媒の調製〕粉末 T565 g と、粉末 F226 g と、酢酸バリウムを BaO 換算で 10 g と、硝酸性アルミナバインダー 9 g と、純水 1000 g とを混合粉碎してスラリーとし、コーゼライト質モノリス担体 (900 セル/2 ミル、1.3 L) に付着さ *

*せ、乾燥・焼成し、90 g/L をコートした触媒 T0 を得た。更に、粉末 V128 g と、 $\text{Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$ 粉末 200 g と、硝酸性アルミナバインダー 12 g と、純水 500 g とを混合粉碎してスラリーとし、触媒 T0 に付着させ、乾燥・焼成し、触媒 T0 に 34 g/L をコートした二層構造の触媒 T1 を得た。この触媒 T1 の Pd 担持量は 5.65 g/L、Rh 担持量は、0.51 g/L であった。

【0048】〔触媒仕様〕表 1 に、上記各触媒粉末の主な触媒成分等を示し、また表 2 に、上記各触媒調製により作成した触媒の仕様を示した。

【0049】

【表 1】

触媒粉末	担持貴金属種 (一)	担持濃度 (%)	担持基材
A	Pd	10.0	CeO_2
B	Pd	10.0	$\text{Zr}_{0.1}\text{Ce}_{0.9}\text{O}_2$
C	Pd	10.0	$\text{Zr}_{0.2}\text{Ce}_{0.8}\text{O}_2$
D	Pd	10.0	$\text{Zr}_{0.5}\text{Ce}_{0.5}\text{O}_2$
E	Pd	10.0	$\text{Zr}_{0.8}\text{Ce}_{0.1}\text{O}_2$
F	Pd	5.0	CeO_2
G	Rh	6.0	$\text{Ca}_{0.2}\text{Zr}_{0.8}\text{O}_2$
H	Rh	6.0	$\text{Mg}_{0.1}\text{Zr}_{0.9}\text{O}_2$
I	Rh	6.0	$\text{Ba}_{0.1}\text{Zr}_{0.9}\text{O}_2$
J	Rh	6.0	$\text{Sr}_{0.2}\text{Zr}_{0.8}\text{O}_2$
K	Rh	6.0	$\text{Ca}_{0.1}\text{Mg}_{0.1}\text{Zr}_{0.8}\text{O}_2$
L	Rh	6.0	$\text{Ca}_{0.1}\text{Ba}_{0.05}\text{Mg}_{0.05}\text{Zr}_{0.8}\text{O}_2$
M	Rh	6.0	$\text{Ca}_{0.01}\text{Zr}_{0.99}\text{O}_2$
N	Rh	6.0	$\text{Ca}_{0.5}\text{Zr}_{0.5}\text{O}_2$
O	Pd	15.0	Al_2O_3
P	Pd	15.0	Ce3%- Al_2O_3
Q	Pd	15.0	Zr3%- Al_2O_3
R	Pd	15.0	La3%- Al_2O_3
S	Pd	15.0	Zr10%- Al_2O_3
T	Pd	8.0	Al_2O_3
U	Pt	6.0	Al_2O_3
V	Rh	4.0	Al_2O_3

【0050】

【表 2】

触媒	触媒構造	貴金属担持量(g/L)				(g/L) 7%Pt	(g/L) 7%Pt±0.5	HC吸着材層	第一層	第二層	第三層
AG1	図3	Pd	Pt	Rh		—	—	β(Si/2AF=25)	A	G	—
AG2	図3	7.06	—	3.53		—	—	β(Si/2AF=15)	A	G	—
AG3	図3	7.06	—	3.53		—	—	β(Si/2AF=300)	A	G	—
AG4	図3	7.06	—	3.53		—	—	β(=25)+ZSM5(30)	A	G	—
AG5	図3	7.06	—	3.53		—	—	β(=25)+USY(=15)	A	G	—
AG6	図3	7.06	—	3.53		—	—	AgP-β(=25)	A	G	—
AG7	図3	7.06	—	3.53		—	—	Pd-β(=25)	A	G	—
BG	図3	7.06	—	3.53		—	—	β(=25)	B	G	—
CG	図3	7.06	—	3.53		—	—	β(=25)	C	G	—
DG	図3	7.06	—	3.53		—	—	β(=25)	D	G	—
EG	図3	7.06	—	3.53		—	—	β(=25)	E	G	—
FG	図3	7.06	—	3.53		—	—	β(=25)	F	G	—
BAH	図3	14.12	—	3.53		—	—	β(=25)	B+A	H	—
BAI	図3	14.12	—	3.53		—	—	β(=25)	B+A	I	—
BAJ	図3	14.12	—	3.53		—	—	β(=25)	B+A	J	—
BAK	図3	14.12	—	3.53		—	—	β+ZSM5	B+A	K	—
BAL	図3	14.12	—	3.53		—	—	β+USY	B+A	L	—
BAM	図3	14.12	—	3.53		—	—	AgP-β	B+A	M	—
BAN	図3	14.12	—	3.53		—	—	Pd-β	B+A	N	—
OBAL	図4	21.18	—	3.53		—	—	β	O	B+A	L
PBBK	図4	21.18	—	3.53		—	—	β	P	2×B	K
QBCJ	図4	21.18	—	3.53		—	—	β+ZSM5	Q	B+C	J
RBDJ	図4	21.18	—	3.53		—	—	β+USY	R	B+D	I
SBEH	図4	21.18	—	3.53		—	—	AgP-β	S	B+E	H
OBFG	図4	21.18	—	3.53		—	—	Pd-β	O	B+F	G
BGN1	図5	12.0	3.18	3.88		(Na ₂ O) ₂	(BaO) ₂₀	β	B	G	T+U+V
N1	第一層	4.94	3.18	0.35		(Na ₂ O) ₂	(BaO) ₂₀				
N2	第一層	4.94	3.18	0.35		(MgO) ₁₀	(BaO) ₁₀				
T1	第一層	5.85	—	0.51		—	(BaO) ₁₀				

【0051】＜各触媒の性能評価＞性能評価は車両評価を行い、北米でのテストモードであるFTP-75モード(LA-4)にて走行した時の各排気ガス成分の排出量の測定を行った。本性能評価に用いた排気ガス浄化システムの構成を図6に示す。該システムは、触媒1及び2、エンジン10、燃料噴射装置11、O₂センサー1*

$$\text{残存率} = \{1 - (\text{NO}_x \text{ 浄化触媒出口の排出ガス中のHC、CO、NO}_x \text{ 排出量}) / (\text{エンジンアウトの排出ガス中のHC、CO、NO}_x \text{ 排出量})\} \times 100 (\%) \cdots \textcircled{7}$$

(上記排出ガス中のHC、CO、NO_x排出量は、上記の車両評価モードを走行したときの排出量を示す)で表される計算式で調べた。また、表3は、上記の車両評価モードで走行する場合のスタート直後の走行部分、具体的にはFTP-75モードのスタート後、約200秒までの走行部分を除いた部分のNO_x、HCの各成分の平

*2、ECU13から成る。車両には排ガス流路上流側の触媒1に表3に示した触媒を配置し、その下流側の触媒2に上記NO_x浄化用触媒であるN1又はN2を配置し、実施例1～30及び比較例1とした。排気ガスを上記システムにより浄化し、HC、CO及びNO_xの残存率を次式⑦

均濃度を用いて計算した値である。また、HC濃度も同様に平均濃度を用いて計算した。スタート直後の走行部分を除いたのは、エンジンスタート直後に未燃焼のHCが排出され、HC濃度が高くなってしまい、正しく評価できないからである。なお、性能評価は、以下に示す条件で行った。

【0052】

(耐久条件)

エンジン排気量 3000cc

燃料 日石ダッシュガソリン (Pb=0mg/usg、

S=30ppm以下)

触媒入口ガス温度 650℃

耐久時間 50時間

【0053】

(性能評価条件)

触媒容量 触媒1:本発明の触媒 1.3L

触媒2:NOx浄化触媒 1.3L

評価車両 日産自動車株式会社製 直噴1.8Lエンジン

【0054】得られた結果を表3に示した。

【表3】

【0055】

	搭載位置		残存率 (%)		
	1 触媒	2 触媒	HC	CO	NOx
実施例1	AG1	N1	1.3	1.9	2.4
実施例2	AG2	N1	1.2	1.8	2.2
実施例3	AG3	N1	1.1	1.7	2.1
実施例4	AG4	N1	1.1	1.8	1.9
実施例5	AG5	N1	1.2	1.8	2.0
実施例6	AG6	N1	1.2	1.7	2.0
実施例7	AG7	N1	1.2	1.8	2.1
実施例8	BG	N1	1.2	1.7	1.9
実施例9	CG	N1	1.3	1.8	2.1
実施例10	DG	N1	1.3	1.6	2.2
実施例11	EG	N1	1.2	1.7	2.0
実施例12	FG	N1	1.2	1.8	2.1
実施例13	BAH	N1	1.1	1.9	1.9
実施例14	BAI	N1	1.1	1.8	1.9
実施例15	BAJ	N1	1.1	1.8	2.0
実施例16	BAK	N1	1.2	1.8	2.0
実施例17	BAL	N1	1.1	1.9	2.1
実施例18	BAM	N1	1.2	1.8	2.1
実施例19	BAN	N1	1.3	1.8	2.2
実施例20	OBAL	N1	1.4	2.0	2.2
実施例21	PBBK	N1	1.2	1.8	2.1
実施例22	QBCJ	N1	1.1	1.9	1.9
実施例23	RBDI	N1	1.1	1.8	1.9
実施例24	SBEH	N1	1.1	1.8	2.0
実施例25	OBFG	N1	1.2	1.8	2.0
実施例26	BGN1	N1	1.3	2.4	2.2
実施例27	AG1	N2	1.2	1.7	2.0
実施例28	BG1	N2	1.3	1.6	2.1
実施例29	BAH	N2	1.2	1.7	2.1
実施例30	OBFG	N2	1.1	1.8	2.0
比較例1	T1	N1	4.2	7.1	7.3

【0056】

【発明の効果】以上、説明したように、本発明によれ

ば、特定のHC改質処理とCO水蒸気改質処理等を行っ

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てH₂を生成し、このH₂をNOx還元剤とすることに

より、酸素過剰雰囲気下において、 H_2 を還元剤として NO_x を高効率で浄化し、且つ、未浄化で排出されていたHC、CO成分、特にエンジン始動後の低温域でのHCを著しく低減し、しかも燃費向上効果の高い排気ガス浄化用触媒を提供することができる。

【図面の簡単な説明】

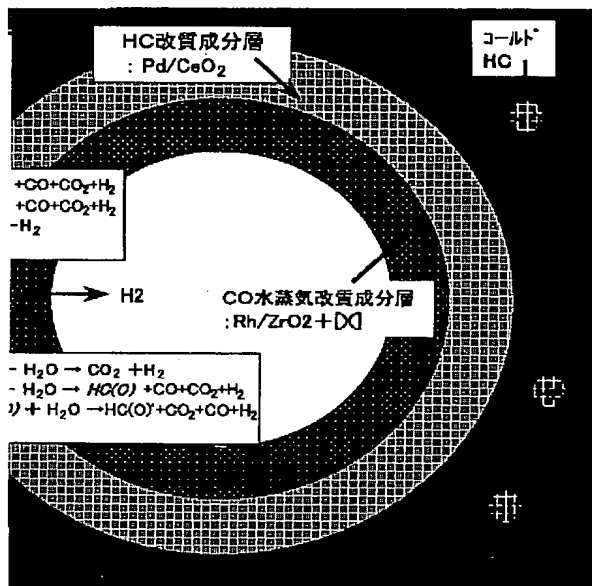
【図1】本発明の排気ガス浄化用触媒の一例を示す横断面図である。

【図2】本発明の排気ガス浄化用触媒の他の例を示す縦断面図である。

【図3】本発明の排気ガス浄化用触媒の他の例を示す縦断面図である。

【図4】本発明の排気ガス浄化用触媒の他の例を示す縦*

【図1】



* 断面図である。

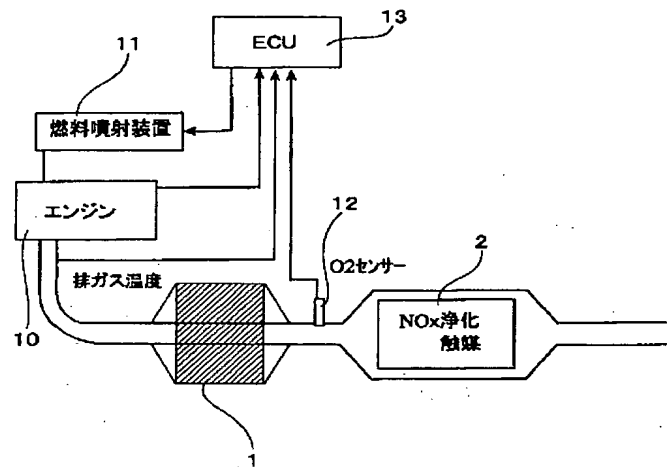
【図5】本発明の排気ガス浄化用触媒の他の例を示す縦断面図である。

【図6】排気ガス浄化用触媒を用いたシステムを示すシステム構成図である。

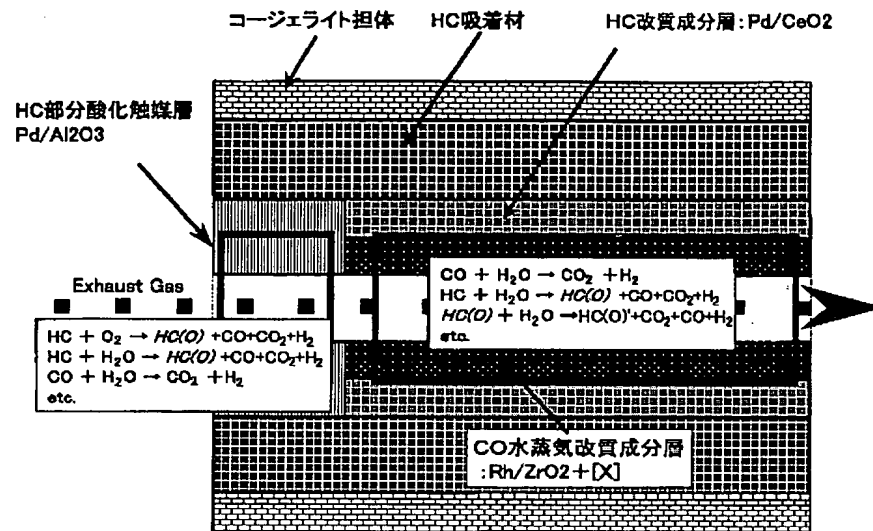
【符号の説明】

- | | |
|----|---------------------|
| 1 | 触媒 |
| 2 | 触媒 |
| 10 | エンジン |
| 11 | 燃料噴射装置 |
| 12 | O ₂ センサー |
| 13 | ECU |

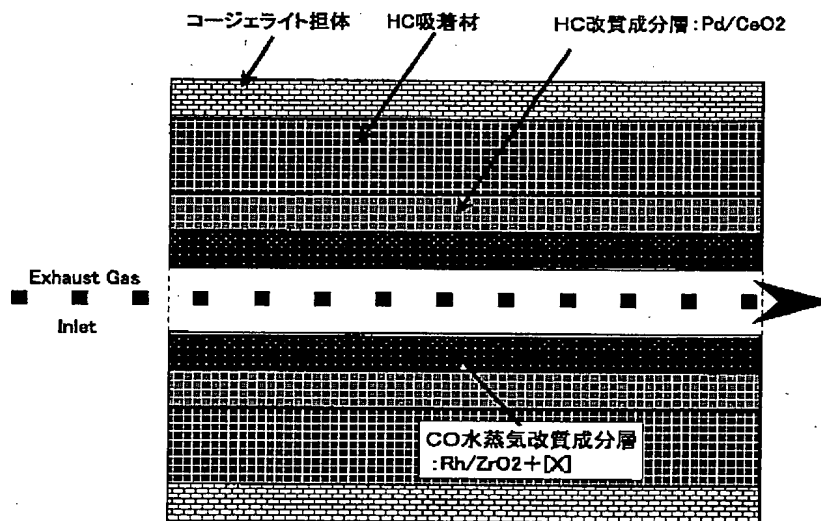
【図6】



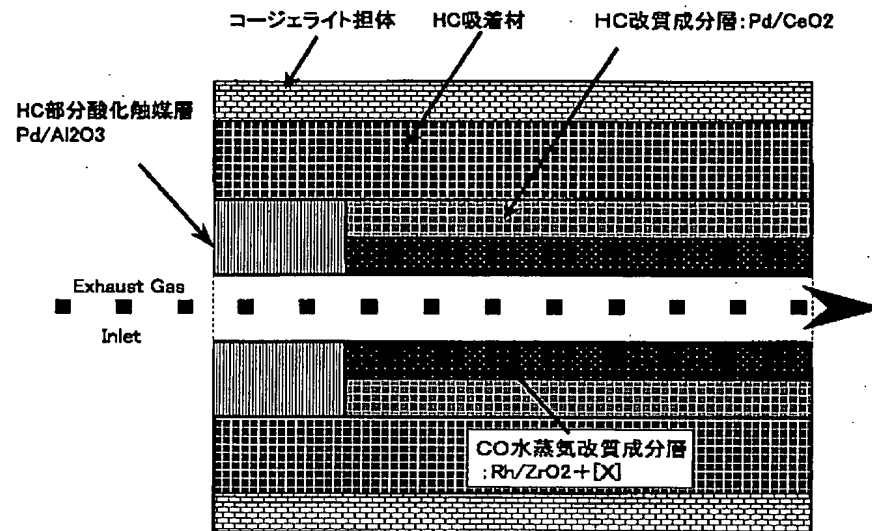
【図2】



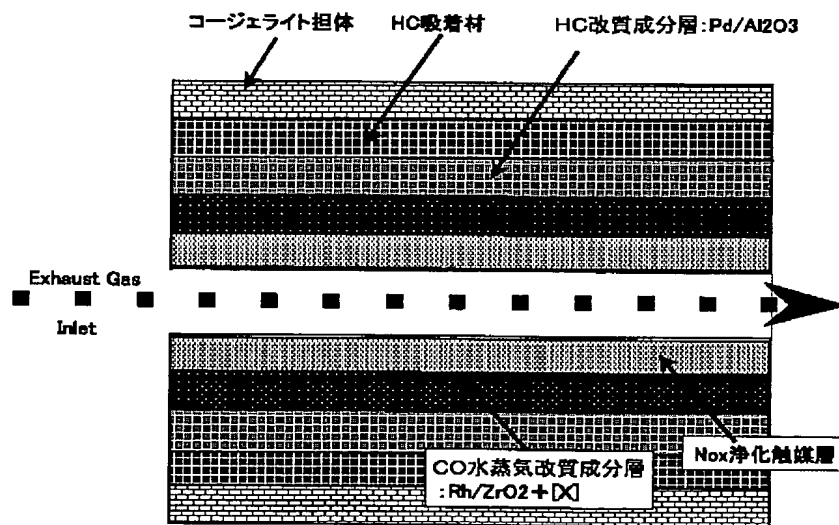
【図3】



【図4】



【図5】



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(54) EXHAUST GAS CLEANING CATALYST

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an exhaust gas cleaning catalyst with which NOx can be cleaned with high efficiency by using H₂ as a reducing agent under an oxygen-excess atmosphere, an HC component and CO component to be not cleaned and discharged in a usual catalyst can be reduced and particularly the HC component can be remarkably reduced in a low temperature region just after an engine is started and which gives highly fuel-efficient effect.

SOLUTION: This catalyst is obtained by layering a zeolite-containing HC adsorbing layer on an integrated structure type carrier and layering a hydrogen generating and nitrogen oxides cleaning catalyst layer, where hydrogen is generated from hydrocarbon and/or carbon monoxide contained in the exhaust gas and nitrogen oxides are cleaned by using the generated hydrogen, on the HC adsorbing layer.

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CLAIMS

[Claim(s)]

[Claim 1] A catalyst for exhaust gas purification which carries out the laminating of the HC adsorption layer on integral-construction mold support, is a catalyst for exhaust gas purification which carries out the laminating of H₂ generation and the NO_x purification catalyst bed, and changes on this, and is characterized by the above-mentioned H₂ generation and NO_x purification catalyst bed purifying nitrogen oxides using hydrogen which generated and generated hydrogen from a hydrocarbon and/or a carbon monoxide.

[Claim 2] A catalyst for exhaust gas purification according to claim 1 characterized by to generate hydrogen from a hydrocarbon from which the above-mentioned H₂ generation and NO_x purification catalyst bed stick to the above-mentioned HC adsorption layer at the time of cold operation of the target internal combustion engine, and is desorbed in a warm-up process, a hydrocarbon discharged after a warm-up of an internal combustion engine, and/or a carbon monoxide, and to purify nitrogen oxides using these hydrogen, carbonization carbon in exhaust gas, and/or a carbon monoxide.

[Claim 3] The above-mentioned H₂ generation and NO_x purification catalyst bed contain H₂ generation catalyst component and an NO_x purification catalyst component. The above-mentioned H₂ generation catalyst component HC reforming component which reforms a hydrocarbon and generates hydrogen, and CO reforming component which carries out steam reforming of CO and generates hydrogen are contained. The above-mentioned HC reforming component A cerium oxide which supported palladium is contained. The above-mentioned CO reforming component The above-mentioned HC reforming component and the above-mentioned CO reforming component are mixed for the above-mentioned H₂ generation and NO_x purification catalyst bed by containing a zirconic acid ghost which supported a rhodium, and the same layer is formed, The laminating of the above-mentioned CO reforming component is carried out on the above-mentioned HC reforming component, Or a catalyst for exhaust gas purification according to claim 1 or 2 characterized by consisting of either of the above-mentioned HC reforming component being arranged at the upstream of a flow direction of exhaust gas, and the above-mentioned CO reforming component being arranged at the downstream.

[Claim 4] A catalyst for exhaust gas purification given in any one term of claims 1-3 characterized by including a catalyst bed in which catalyst entrance-side portions of the above-mentioned H₂ generation and NO_x purification catalyst bed contain an alumina which supported palladium.

[Claim 5] exhaust gas of a catalyst entrance when purifying the above-mentioned nitrogen oxides -- amount of hydrogen/-- all -- a catalyst for exhaust gas purification given in any one term of claims 1-4 characterized by satisfying a gas presentation expressed with amount \geq of reduction components 0.3.

[Claim 6] A zirconic acid ghost which supported the above-mentioned rhodium contains alkaline earth metal, and the presentation is degree type aZr_bO_c . -- aZr_bO_c (X in a formula) At least one sort of elements chosen from a group which consists of magnesium, calcium, strontium, and barium, and a and b an oxygen atomic number required for a rate of an atomic ratio and c to satisfy a valence of X and Zr -- being shown -- $a = 0.01$ to 0.5 , $b = 0.5$ to 0.99 , and $a + b = 1$ -- filling -- a catalyst for exhaust gas purification given in any one term of claims 3-5 characterized by what is expressed.

[Claim 7] A catalyst for exhaust gas purification given in any one term of claims 4-6 to which at least one catalyst bed chosen from a group which consists of a catalyst bed containing an alumina which supported the above-mentioned HC adsorption layer, a catalyst bed containing the above-mentioned HC reforming component, a catalyst bed containing the above-mentioned CO reforming component, and the above-mentioned palladium is characterized by containing an NO_x purification catalyst component.

[Claim 8] At least one catalyst bed chosen from a group which consists of a catalyst bed containing an alumina which supported the above-mentioned HC adsorption layer, a catalyst bed containing the above-mentioned HC reforming component, a catalyst bed containing the above-mentioned CO reforming component, and the above-mentioned

palladium A catalyst for exhaust gas purification given in any one term of claims 4-7 characterized by containing at least one sort of NOx reduction components chosen from a group which consists of palladium, platinum, a rhodium, an alumina, alkali metal, and alkaline earth metal.

[Claim 9] A catalyst for exhaust gas purification according to claim 8 characterized by the above-mentioned alkali metal and/or an alkaline earth metal containing at least one sort of elements chosen from a group which consists of a potassium, caesium, magnesium, calcium, and barium.

[Claim 10] the above-mentioned HC adsorption layer -- Si / 2aluminum ratio -- a catalyst for exhaust gas purification given in any one term of claims 1-9 characterized by containing an H mold beta-zeolite of =10-500.

[Claim 11] A catalyst for exhaust gas purification given in any one term of claims 1-10 characterized by the above-mentioned HC adsorption layer containing at least one sort of zeolites chosen from a group which consists of an H mold beta-zeolite, MFI and Y mold, USY, and mordenite.

[Claim 12] A catalyst for exhaust gas purification according to claim 10 or 11 characterized by a zeolite of the above-mentioned HC adsorption layer containing at least one sort of elements chosen from a group which consists of palladium, magnesium, calcium, strontium, barium, silver, an yttrium, a lanthanum, a cerium, neodymium, Lynn, boron, and a zirconium.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the catalyst for emission gas purification, and relates to the catalyst for exhaust gas purification which purifies the nitrogen oxides (NOx) in hyperoxia exhaust gas with a well head in details further.

[0002]

[Description of the Prior Art] Conventionally, the catalyst which performs oxidation of a carbon monoxide (CO) and a hydrocarbon (HC) and reduction of NOx to coincidence is used widely as a catalyst for exhaust gas purification of internal combustion engines, such as an automobile. What added base metal oxides, such as rare earth metals, such as a cerium (Ce) and a lanthanum (La), and nickel (nickel), as a co-catalyst component as such a catalyst if needed [of having made the alumina coat layer on fireproof support supporting noble metals, such as palladium (Pd), and platinum (Pt), a rhodium (Rh), / the thing and if needed] is indicated (JP,58-20307,A). The catalyst currently indicated by the above-mentioned official report is strongly influenced of exhaust gas temperature and an engine setting air-fuel ratio, especially when an internal combustion engine's exhaust gas is hyperoxia, it cannot purify NOx. By carrying out occlusion of NOx to the patent printing No. 2600429 official report, when exhaust gas is hyperoxia, reducing an oxygen density after that and making it a rich ambient atmosphere temporarily as a method of purifying nitrogen oxides, when such an internal combustion engine's exhaust gas is hyperoxia, NOx by which occlusion was carried out is emitted and the method by the so-called rich spike of carrying out purification processing is indicated.

[0003]

[Problem(s) to be Solved by the Invention] however, by the method by rich spike which is indicated in the above-mentioned official report In order to carry out the reduction reaction of NOx under the conditions to which the oxygen density in exhaust gas needed to be periodically reduced also in the operating range of hyperoxia, and the oxygen density fell further A lot of HC and COs as a reducing agent needed to be supplied, and the technical problem that the effect of the improvement in fuel consumption by running by hyperoxia was not fully acquired occurred.

[0004] Furthermore, although a lot of alkali metals and alkaline-earth-metal elements are made to contain in order to carry out occlusion of NOx in a hyperoxia ambient atmosphere for this reason, the oxidation activity at the time of the low temperature of Pt, Pd, and Rh which are an active metal is no longer acquired fully. Moreover, in order to fully purify HC and CO component which were not consumed at an NOx purification reaction, it is necessary to make it purify by oxidation reaction, or to arrange and purify a three way component catalyst in the latter part of an NOx purification catalyst. However, in such a catalyst system, since the catalyst which purifies HC and CO was arranged in the latter part of an exhaust-stream way, sufficient HC and the purification engine performance of CO were not obtained, but the technical problem were difficult also had HC and CO component purification which are discharged especially immediately after engine starting.

[0005] The place which this invention is made in view of the technical problem which such conventional technology has, and is made into the purpose purifies NOx with a well head under a hyperoxia ambient atmosphere, and reduces remarkably HC in HC discharged by un-purifying, CO component, especially the low-temperature region after engine starting, and is to offer the high catalyst for exhaust gas purification of the improvement effect in fuel consumption moreover.

[0006]

[Means for Solving the Problem] That the above-mentioned technical problem should be solved, this invention person came to complete a header and this invention for the above-mentioned technical problem being solvable by performing specific HC reforming processing, CO steam-reforming processing, etc., generating H2, and using these H2 as an NOx

reducing agent, as a result of inquiring wholeheartedly.

[0007] That is, a catalyst for exhaust gas purification of this invention carries out the laminating of the HC adsorption layer on integral-construction mold support, is a catalyst for exhaust gas purification which carries out the laminating of H₂ generation and the NO_x purification catalyst bed, and changes on this, and is characterized by the above-mentioned H₂ generation and NO_x purification catalyst bed purifying nitrogen oxides using hydrogen which generated and generated hydrogen from a hydrocarbon and/or a carbon monoxide.

[0008] Moreover, a suitable gestalt of a catalyst for exhaust gas purification of this invention generates hydrogen from a hydrocarbon from which the above-mentioned H₂ generation and NO_x purification catalyst bed stick to the above-mentioned HC adsorption layer at the time of cold operation of the target internal combustion engine, and is desorb in a warm-up process, a hydrocarbon discharge after a warm-up of an internal combustion engine, and/or a carbon monoxide, and is characterize by to purify nitrogen oxides using these hydrogen, carbonization carbon in exhaust gas, and/or a carbon monoxide.

[0009] Furthermore, other suitable configurations of a catalyst for exhaust gas purification of this invention. The above-mentioned H₂ generation and NO_x purification catalyst bed contain H₂ generation catalyst component and an NO_x purification catalyst component. The above-mentioned H₂ generation catalyst component HC reforming component which reforms a hydrocarbon and generates hydrogen, and CO reforming component which carries out steam reforming of CO and generates hydrogen are contained. The above-mentioned HC reforming component A cerium oxide which supported palladium is contained. The above-mentioned CO reforming component The above-mentioned HC reforming component and the above-mentioned CO reforming component are mixed for the above-mentioned H₂ generation and NO_x purification catalyst bed by containing a zirconic acid support which supported a rhodium, and the same layer is formed, It is characterized by consisting of either that the laminating of the above-mentioned CO reforming component is carried out on the above-mentioned HC reforming component, or that the above-mentioned HC reforming component is arranged at the upstream of a flow direction of exhaust gas, and the above-mentioned CO reforming component is arranged at the downstream.

[0010] Furthermore, other suitable gestalten of a catalyst for exhaust gas purification of this invention are characterized by including a catalyst bed in which catalyst entrance-side portions of the above-mentioned H₂ generation and NO_x purification catalyst bed contain an alumina which supported palladium again.

[0011] moreover, exhaust gas of a catalyst entrance in case a suitable gestalt of further others of a catalyst for exhaust gas purification of this invention purifies the above-mentioned nitrogen oxides -- amount of hydrogen/-- all -- it is characterized by satisfying a gas presentation expressed with amount \geq of reduction components 0.3.

[0012] Furthermore, other suitable gestalten of a catalyst for exhaust gas purification of this invention again A zirconic acid ghost which supported the above-mentioned rhodium contains alkaline earth metal, and the presentation is degree type $[X]_a ZrO_b$. -- $(X \text{ in a formula})$ At least one sort of elements chosen from a group which consists of magnesium, calcium, strontium, and barium, and a and b an oxygen atomic number required for a rate of an atomic ratio and c to satisfy a valence of X and Zr -- being shown -- $a = 0.01 \text{ to } 0.5$, $b = 0.5 \text{ to } 0.99$, and $a+b=1$ -- filling -- it is characterized by what is expressed.

[0013] Moreover, it is characterized by at least one catalyst bed chosen from a group which consists of a catalyst bed containing an alumina with which other suitable gestalten of a catalyst for exhaust gas purification of this invention supported the above-mentioned HC adsorption layer, a catalyst bed containing the above-mentioned HC reforming component, a catalyst bed containing the above-mentioned CO reforming component, and the above-mentioned palladium containing an NOx purification catalyst component.

[0014] Furthermore, other suitable gestalten of a catalyst for exhaust gas purification of this invention again At least one catalyst bed chosen from a group which consists of a catalyst bed containing an alumina which supported the above-mentioned HC adsorption layer, a catalyst bed containing the above-mentioned HC reforming component, a catalyst bed containing the above-mentioned CO reforming component, and the above-mentioned palladium It is characterized by containing at least one sort of NOx reduction components chosen from a group which consists of palladium, platinum, a rhodium, an alumina, alkali metal, and alkaline earth metal.

[0015] moreover, a suitable gestalt of further others of a catalyst for exhaust gas purification of this invention -- the above-mentioned HC adsorption layer -- Si / 2aluminum ratio -- it is characterized by containing an H mold beta-zeolite of =10-500.

[0016] Furthermore, other suitable gestalten of a catalyst for exhaust gas purification of this invention are characterized by the above-mentioned HC adsorption layer containing at least one sort of zeolites chosen from a group which consists of an H mold beta-zeolite, MFI and Y mold, USY, and mordenite again.

[0017] Moreover, other suitable gestalten of a catalyst for exhaust gas purification of this invention are characterized by

a zeolite of the above-mentioned HC adsorption layer containing at least one sort of elements chosen from a group which consists of palladium, magnesium, calcium, strontium, barium, silver, an yttrium, a lanthanum, a cerium, neodymium, Lanthanum, boron, and a zirconium.

[0018]

[Embodiment of the Invention] Hereafter, the catalyst for exhaust gas purification of this invention is explained to details. In addition, "%", unless it mentions specially, mass percentage is shown. On integral-construction mold support, the catalyst for exhaust gas purification of this invention carries out the laminating of the HC adsorption layer, on this, carries out the laminating of H₂ generation and the NO_x purification catalyst bed, and changes.

[0019] A zeolite with cold HC adsorption capacity is used as a principal component, the above-mentioned HC adsorption layer is immediately after the time of cold operation of the target internal combustion engine, i.e., engine starting, when a catalyst is still low temperature, it adsorbs HC, and when it is in a catalyst warming-up process (150-300 degrees C), it is desorbed from HC. Next, by the HC-CO reforming reaction mentioned later, H₂ generation and the NO_x purification catalyst bed by which the laminating is carried out to the above-mentioned HC adsorption layer can generate H₂ from Desorption HC, and can generate H₂ further also from HC and/or CO which are discharged at the time of steady operation of an internal combustion engine. These H₂ generated often reacts with NO_x in exhaust gas as an NO_x reducing agent. It is guessed that it can purify efficiently NO_x discharged in a catalyst warming-up process until it reaches the operation control of a hyperoxia ambient atmosphere from immediately after engine starting since the reactivity of H₂ and NO_x is high although temperature does not rise and the NO_x purification catalyst component contained in H₂ generation and an NO_x purification catalyst bed at this time is not fully being activated.

[0020] Generally the above-mentioned HC-CO reforming reaction performed by the above-mentioned H₂ generation and NO_x purification catalyst bed can be divided into the reforming reaction and CO steam-reforming reaction of HC. This HC reforming reaction Moreover, degree type ** and ** $HC+O_2 \rightarrow HC(O)+CO+CO_2+H_2$ $O+H_2 \rightarrow HC(O)+CO+CO_2+H_2$ -- ** $HC+H_2 O \rightarrow HC(O)+CO+CO_2+H_2$ -- It is thought that it is expressed with ** (HC in a formula (O) shows HC after a reforming reaction), and the above-mentioned CO steam-reforming reaction is expressed with degree type ** $CO+H_2 O \rightarrow CO_2+H_2$ --**.

[0021] It makes it face that the above-mentioned HC-CO reforming reaction generates H₂, and the laminating of the above-mentioned H₂ generation and NO_x purification catalyst bed is carried out on the above-mentioned HC adsorption layer. Although HC reforming component layer which CO reforming component which carries out steam reforming of HC reforming component and CO which reform HC and generate H₂, and generates H₂ is mixed, and this layer forms one layer, or contains HC reforming component, and CO steam-reforming layer containing CO reforming component form the multilayer by which the laminating is carried out It is desirable to take the structure which carried out the laminating of the CO steam-reforming component layer on HC reforming component layer especially. As shown in drawing 1, reforming of the HC which the above-mentioned HC adsorption layer was adsorbed and was emitted from the above-mentioned HC adsorption layer in the catalyst warming-up process immediately after engine starting is first carried out to a partial oxidation object, HC (O), and CO and H₂ in the above-mentioned HC reforming component layer, and conversion of CO is further carried out to H₂ in the above-mentioned CO steam-reforming component layer. Since HC and CO which are contained in exhaust gas in a catalyst warming-up process like **** by taking such structure are reformed and H₂ can be generated, also in a hyperoxia operating range, H₂ is supplied and after catalyst warming up can carry out purification processing of NO_x. In addition, since conversion of the HC should just be carried out in the order of HC reforming reaction and CO steam-reforming reaction, the above-mentioned HC reforming component layer and the above-mentioned CO steam-reforming component layer may take tandem arrangement along exhaust gas passage, and are not limited to especially the above-mentioned multilayer structure.

[0022] Furthermore, it is desirable to make the above-mentioned HC reforming component layer contain the cerium oxide which supported Pd, in order to reform HC and to generate H₂, and in order to carry out steam reforming of CO and to generate H₂, it is desirable to make the above-mentioned CO steam-reforming component layer contain the zirconic acid ghost which supported Rh. When exhaust gas is passed in the catalyst for emission gas purification of this invention by making these noble metals and oxides contain, it sets in the above-mentioned HC reforming component layer. Mainly Degree type **-** $HC+O_2 \rightarrow HC(O)+CO+CO_2+H_2$ -- ** $HC+H_2 O \rightarrow HC(O)+CO+CO_2+H_2$ -- ** $CO+H_2 O \rightarrow CO_2+H_2$ -- The reaction of ** occurs and it sets in the above-mentioned CO steam-reforming component layer. Mainly Degree type **, **, and ** $CO+H_2 O \rightarrow CO_2+H_2$ -- ** $HC+H_2 O \rightarrow HC(O) + CO+CO_2+H_2$ --** $HC(O) + H \rightarrow$ the reaction of $2 O \rightarrow HC(O)'+CO_2+CO+H_2$ --** occurs, and while H₂ is generated, an exhaust gas component, especially HC and CO are purified.

[0023] Furthermore, when the above-mentioned H₂ generation and NO_x purification catalyst bed contain not only the above H₂ generation catalyst components but an NO_x purification catalyst component, while generating H₂ which is an

NOx reducing agent with one catalyst again, NOx can be purified efficiently.

[0024] Furthermore, in order to make H₂ generate intentionally from HC in exhaust gas, and CO after engine-warm process termination, as for the catalyst for exhaust gas purification of this invention, it is desirable that the catalyst bed in which a part of above-mentioned H₂ generation catalyst of the upstream, i.e., this catalyst entrance-side portion, contains the alumina which supported Pd is included. For example, the laminating of the HC partial oxidation catalyst containing Pd support alumina is carried out to the catalyst entrance side on the above-mentioned HC adsorption catalyst bed as one suitable gestalt of the catalyst for exhaust gas purification of this invention, and the structure where the laminating of HC reforming component layer which contains Pd support cerium oxide on the above-mentioned HC adsorption layer, and the CO steam-reforming component layer containing Rh support zirconic acid ghost is carried out is listed to the downstream. Although the above-mentioned structure is shown in drawing 2, especially the catalyst for emission gas purification of this invention is not limited to this.

[0025] Moreover, as shown in drawing 2, it sets after catalyst warming up. By the catalyst bed containing the alumina which supported Pd arranged into this above-mentioned catalyst entrance-side portion Conversion of the HC contained by the partial oxidation reaction in exhaust gas is carried out to HC(O) and CO. Next, H₂ generation is promoted by the reforming reaction of HC (O) in the above-mentioned HC reforming component layer, and it is guessed that CO₂ and H₂ are subsequently generated by the steam-reforming reaction from CO and H₂O in the above-mentioned CO steam-reforming component layer. Therefore, in this invention, it continues at an above-mentioned catalyst warming-up process, after catalyst warming up can supply H₂, and even if it is under a hyperoxia ambient atmosphere, it is thought that the reduction purification of NOx can be carried out.

[0026] thus, instead of [of HC and CO which were mainly used from the former as a reduction component used for NOx purification in the catalyst for exhaust gas purification of this invention] -- or the exhaust gas of the catalyst entrance when ** using H₂ being made in addition to this, but carrying out NOx purification further -- H₂ amount/-- all -- it is desirable to satisfy the gas presentation expressed with amount \geq of reduction components 0.3. If this gas presentation is satisfied, since H₂ concentration in exhaust gas will become high, the still higher NOx purification engine performance can be obtained.

[0027] namely, H₂ ratio in the exhaust gas at the time of using the exhaust gas and exhaust gas catalyst from an automobile engine conventionally -- H₂ amount/-- all -- although it was amount $<$ of reduction components 0.3, the ratio of H₂ was low and it was impossible to have used H₂ effectively as a reduction component, in this invention, this ratio is increased and H₂ is used effectively. in addition, the above-mentioned exhaust gas presentation -- H₂ amount/-- all -- although it will come out enough if amount \geq of reduction components 0.3 are satisfied -- H₂ amount/-- all -- it is still more desirable to be referred to as amount \geq of reduction components 0.5.

[0028] Moreover, it is desirable that the above-mentioned Rh support zirconic acid ghost contains alkaline earth metal, and changes in order to maintain the oxidation state of Above Rh in the condition of having been suitable for CO steam-reforming reaction, in the above-mentioned CO steam-reforming component layer, and the presentation is degree type $aXbZrc$. -- It is expressed with **. a shows an oxygen atomic number required for the rate of an atomic ratio of this element and b to satisfy the rate of an atomic ratio of Zr, and for c satisfy the valence of this element and Zr by X of the above-mentioned formula ** showing the element concerning the combination of Mg, calcium, Sr or Ba(s), and such arbitration, and $a = 0.01$ to 0.5 , $b = 0.5$ to 0.99 , and $a + b = 1$ are filled. If the above-mentioned alkaline earth metal is made to contain, high catalytic activity can be acquired from the first stage to until after durability.

[0029] Furthermore, as for the catalyst bed concerning the combination of the catalyst beds containing the alumina which supported the above-mentioned HC adsorption layer, the above-mentioned above-mentioned H₂ generation and NOx purification catalyst bed, or Above Pd, and such arbitration, it is desirable to contain an NOx purification catalyst component. That is, all of the catalyst bed containing the alumina which supported Pd arranged at the above-mentioned HC adsorption layer, HC reforming component layer, CO steam-reforming component layer, and this catalyst entrance-side portion can be made to contain Pd and Pt which are an NOx purification catalyst component, Rh, etc. While making H₂ generate in a catalyst warming-up process by making an NOx purification catalyst component contain, NOx discharged in a catalyst warming-up process can be purified efficiently, and NOx by which after catalyst warming up is discharged at the time of the operation control under a hyperoxia ambient atmosphere can be purified further efficiently. In addition, not only making each catalyst bed contain an NOx purification catalyst component as mentioned above but it may carry out the laminating of the NOx purification catalyst bed further on the above-mentioned H₂ generation and NOx purification catalyst bed, and you may carry out the laminating of the NOx purification catalyst bed, without making each catalyst bed contain an NOx purification catalyst component. Furthermore, tandem arrangement of the catalyst for NOx purification may be carried out for the catalyst for emission gas purification of this invention at an emission style side on the street at the downstream.

[0030] Moreover, especially the catalyst bed concerning the combination of the catalyst beds containing the alumina which supported Pd arranged at the above-mentioned HC adsorption layer, HC reforming component layer, CO steam-reforming component layer, or the above-mentioned catalyst entrance-side portion, and such arbitration can contain the NOx purification catalyst component concerning the combination of Pd, Pt, Rh, an alumina, alkali metal or alkaline earth metal, and such arbitration. By containing these NOx purification components, NOx by which it is discharged from an engine from immediately after engine starting till steady operation control of a hyperoxia ambient atmosphere can be purified efficiently. In addition, although the metal concerning the combination of a potassium (K), caesium (Cs), magnesium (Mg), calcium (calcium) or barium (Ba), and such arbitration can be mentioned as the above-mentioned alkali metal and/or an alkaline earth metal, it is not limited to these.

[0031] Furthermore, if the above-mentioned alkali metal and the alkaline-earth-metal content in each above-mentioned whole catalyst bed turn into this 80% of the weight or more of metal content total amount in the catalyst for emission gas purification of this invention, NOx discharged in the Kohl Doreen region is absorbable, but if it becomes less than 80% of the weight, sufficient NOx absorbing power will not be acquired. Moreover, in order for each above-mentioned whole catalyst bed to contain 80% of the weight or more of the total amount of alkali metal and alkaline earth metal, it is desirable that alkali metal and/or alkaline earth metal are insoluble compounds and/or poorly soluble compounds.

[0032] Moreover, although the zeolite used by the above-mentioned HC adsorption layer can be used choosing it suitably from well-known zeolites, it is desirable to choose from ordinary temperature especially what has sufficient HC adsorption capacity and has high endurance even if it is under a water existence ambient atmosphere moreover at a comparatively high temperature. As such a zeolite, typically, Si / 2aluminum ratio is not limited to especially this, although the H mold beta-zeolite of 10-500 is mentioned. Since adsorption inhibition of the moisture with which Si / 2aluminum ratio coexists in exhaust gas in less than ten zeolite is serious, HC cannot be adsorbed effectively but HC adsorption capacity may fall in the zeolite with which Si / 2aluminum ratio exceeds 500.

[0033] Furthermore, according to the exhaust gas component discharged from an engine, the zeolite concerning the combination of MFI and Y mold with which pore size differs from pore structure, USY or mordenites, and such arbitration is chosen, and if it mixes and uses for the above-mentioned H mold beta-zeolite, HC in exhaust gas can be adsorbed efficiently.

[0034] In addition, although it has HC adsorption capacity sufficient also with the above-mentioned H mold beta-zeolite To the various above-mentioned zeolites, Pd, Mg, calcium, strontium (Sr), Ba, silver (Ag), an yttrium (Y), La and Ce, neodymium (Nd), HC adsorbent ability and HC desorption control ability can be further improved by supporting the element concerning the combination of Lynn (P), boron (B) or zirconiums (Zr), and such arbitration using the usual methods, such as an ion-exchange method, an impregnation method, and dip coating.

[0035] Moreover, there is for example, honeycomb support in the up Norikazu object structured type catalyst support of the catalyst for exhaust gas purification of this invention, and, generally many things of quality of cordierite, such as a ceramic, are used for it as a honeycomb material. However, it may not be restricted to this, but the honeycomb material which consists of metallic materials, such as ferrite system stainless steel, may be used, and the catalyst component powder itself may be further fabricated in a honeycomb configuration.

[0036]

[Example] Hereafter, although an example and the example of a comparison explain this invention to details further, this invention is not limited to these examples.

[0037] It sank into cerium oxide (CeO₂) powder, the [preparation of catalyst powder of HC reforming component layer] nitric-acid Pd aqueous solution was dried and calcinated, and Pd support cerium oxide powder A was obtained. Pd support concentration of this powder was 10%. Moreover, what set to Powder D and Zr_{0.9}Ce_{0.1}O₂ what set to Powder C and Zr_{0.5}Ce_{0.5}O₂ what used as Powder B the powder which repeated and obtained the same actuation as Powder A, and set it to Zr_{0.2}Ce_{0.8}O₂ was used as Powder E except having been referred to as Zr_{0.1}Ce_{0.9}O₂ instead of CeO₂. Furthermore, the powder which repeated and obtained the same actuation as Powder A was used as Powder F except having made Pd support concentration into 5%.

[0038] It sank into calcium_{0.2}Zr_{0.8}O₂ powder, the [preparation of catalyst powder of CO steam-reforming component layer] nitric-acid Rh aqueous solution was dried and calcinated, and Rh support zirconic acid ghost powder G was obtained. Rh support concentration of this powder was 6%. Instead of calcium_{0.2}Zr_{0.8}O₂ moreover, except having been referred to as Mg_{0.1}Zr_{0.9}O₂ What used as Powder H the powder which repeated and obtained the same actuation as Powder G, and was set to Ba_{0.1}Zr_{0.9}O₂ Powder I What set to Powder J and calcium_{0.1}Mg_{0.1}Zr_{0.8}O₂ what was set to Sr_{0.2}Zr_{0.8}O₂ Powder K What set to Powder M and calcium_{0.5}Zr_{0.5}O₂ what set to Powder L and calcium_{0.01}Zr_{0.99}O₂ what was set to calcium_{0.1}Ba_{0.05}Mg_{0.05}Zr_{0.8}O₂ was used as Powder N.

[0039] It sank into activated-alumina (aluminum 2O₃) powder, the [preparation of catalyst powder of catalyst bed

containing alumina which supported Pd] nitric-acid Pd aqueous solution was dried and calcinated, and Pd support alumina powder O was obtained. Pd support concentration of this powder was 15%. Moreover, except having been referred to as aluminum 2O3 which contains Ce 3% instead of aluminum 2O3 What set what set what used as Powder P the powder which repeated and obtained the same actuation as Powder O, and was set to aluminum 2O3 which contains Zr 3% to aluminum 2O3 which contains Powder Q and La 3% to aluminum 2O3 which contains Powder R and Zr 10% was used as Powder S.

[0040] It sank into aluminum2O3 powder, the [preparation of catalyst powder containing NOx purification catalyst component] nitric-acid Pd aqueous solution was dried and calcinated, and Pd support alumina powder T was obtained. Pd support concentration of this powder T was 8%. It sank into 2Oaluminum3 powder, the dinitrodiammine Pt acid aqueous solution was dried and calcinated, and Pt support alumina powder U was obtained. Pt support concentration of this powder U was 6%. It sank into 2Oaluminum3 powder, the nitric-acid Rh aqueous solution was dried and calcinated, and Rh support alumina powder V was obtained. Rh support concentration of this powder V was 4%.

[0041] After having carried out preferential grinding of [catalyst preparation 1] beta-zeolite (Si/2aluminum=25) 900g, silica sol 100g, and the 1000g of the pure water, having made it into the slurry, making it adhere to the nature monolith support of cordierite (900 cels / 4 mils, 1.3L) and drying and calcinating it, the zeolite catalyst of amount of zeolite coats 100 g/L was acquired. Subsequently, carried out preferential grinding of the 800g of the pure water to powder A706g and nitric-acid nature alumina binder 12g, considered as the slurry, and it was made to adhere to a zeolite catalyst, and dried and calcinated, and the catalyst A which carried out the coat of 72 g/L to the zeolite catalyst was acquired. The amount of Pd support of this catalyst A was 7.06g./L. Furthermore, carried out preferential grinding of the 600g of the pure water to powder G588g and nitric-acid nature alumina binder 12g, considered as the slurry, and it was made to adhere to Catalyst A, and dried and calcinated, and the catalyst AG1 which carried out the coat of 60 g/L to Catalyst A was acquired. The amount of Rh support of this catalyst AG1 was 3.53 g/L. The catalyst AG1 was made into 3 layer structures shown in drawing 3 . Moreover, a repeat and catalysts 2-AG 7 were acquired for the same actuation using HC adsorption material shown in a table 2 instead of beta-zeolite (Si/2aluminum=25).

[0042] Carried out preferential grinding of the 800g of the pure water to [catalyst preparation 2] powder B706g and nitric-acid nature alumina binder 14g, considered as the slurry, and it was made to adhere to the zeolite catalyst which repeated and prepared the same actuation as catalyst preparation 1, and dried and calcinated, and the catalyst B which carried out the coat of 72g / the L to the zeolite catalyst was acquired. The amount of Pd support of this catalyst B was 7.06 g/L. Next, carried out preferential grinding of the 600g of the pure water to powder G588g and nitric-acid nature alumina binder 12g, considered as the slurry, and it was made to adhere to Catalyst B, and dried and calcinated, and the catalyst BG which carried out the coat of 60 g/L to Catalyst B was acquired. The amount of Rh support of this catalyst BG was 3.53 g/L. Catalyst BG was made into 3 layer structures shown in drawing 3 . Moreover, powder C-F was used instead of Powder B, the same actuation was repeated, and Catalysts CG, DG, EG, and FG were acquired.

[0043] The repeat and the zeolite catalyst were acquired for the same actuation as catalyst preparation 1 except having considered as HC adsorption material shown in a table 2 instead of the [catalyst preparation 3] beta-zeolite (Si/2aluminum=25). Next, carried out preferential grinding of the 1500g of the pure water to powder B706g, powder A706g, and nitric-acid nature alumina binder 28g, considered as the slurry, and it was made to adhere to a zeolite catalyst, and dried and calcinated, and the catalyst BA which carried out the coat of 144 g/L to the zeolite catalyst was acquired. The amount of Pd support of this catalyst BA was 14.12 g/L. Furthermore, carried out preferential grinding of the 600g of the pure water to powder H588g and nitric-acid nature alumina binder 12g, considered as the slurry, and it was made to adhere to Catalyst BA, and dried and calcinated, and the catalyst BAH which carried out the coat of 60 g/L to Catalyst BA was acquired. The amount of Rh support of this catalyst BAH was 3.53 g/L. Catalyst BAH was made into 3 layer structures shown in drawing 3 . Moreover, powder I-N was used instead of Powder H, the same actuation was repeated, and Catalysts BAI, BAJ, BAK, BAL, BAM, and BAN were acquired.

[0044] After having carried out preferential grinding of [catalyst preparation 4] beta-zeolite (Si/2aluminum=25) 900g, silica sol 100g, and the 1000g of the pure water, having made it into the slurry, making it adhere to the nature monolith support of cordierite (900 cels / 4 mils, 1.3L) and drying and calcinating it, the zeolite catalyst of amount of zeolite coats 50 g/L was acquired. Carried out preferential grinding of the 500g of the pure water to powder O471g and nitric-acid nature alumina binder 9g, considered as the slurry, this was made to adhere to 1/4 portion of the exhaust gas entrance side of a zeolite catalyst, it dried and calcinated, and the catalyst O1 which carried out the coat of 48 g/L to the zeolite catalyst was acquired. The amount of Pd support of this catalyst O1 was 7.06 g/L. Subsequently, it was made to adhere to 3/4 portion which carries out preferential grinding of the 1000g of the pure water to powder B706g, powder A706g, and nitric-acid nature alumina binder 28g, considers as a slurry, and has not carried out the coat of the catalyst O1, and dried and calcinated, and the catalyst OBA which carried out the coat of 144 g/L was acquired. The total amount of Pd

support of this catalyst OBA was 21.18 g/L. Furthermore, it was made to adhere to 3/4 portion which carries out preferential grinding of the 600g of the pure water to powder L588g and nitric-acid nature alumina binder 12g, considers as a slurry, and has not carried out the coat of the catalyst O1, and dried and calcinated, and the catalyst OBAL which carried out the coat of 60 g/L to Catalyst OBA was acquired. The amount of Rh support of this catalyst OBAL was 3.53 g/L. Catalyst OBAL was made into the structure shown in drawing 4 . Moreover, the zeolite catalyst of amount of zeolite coats 50 g/L was created using HC adsorption material shown in a table 2 instead of beta-zeolite (Si/2aluminum=25), instead of Powder O, powder B-F was used instead of Powder A, powder G-K was used for P-S instead of Powder L, the same actuation was repeated, and Catalysts PBBK, QBCJ, and RBDI, SBEH, and OBFG were obtained.

[0045] Carried out preferential grinding of the 1000g of the pure water to [catalyst preparation 5] powder B706g and nitric-acid nature alumina binder 14g, considered as the slurry, and it was made to adhere to the zeolite catalyst which repeated and obtained the same actuation as the catalyst preparation 4, and dried and calcinated, and catalyst B-2 which carried out the coat of 72 g/L was obtained. The amount of Pd support of this catalyst B-2 was 7.06 g/L. Subsequently, carried out preferential grinding of the 600g of the pure water to powder G588g and nitric-acid nature alumina binder 12g, considered as the slurry, and it was made to adhere to catalyst B-2, and dried and calcinated, and the catalyst BG which carried out the coat of 60 g/L to catalyst B-2 was acquired. The amount of Rh support of this catalyst BG was 3.53 g/L. Furthermore, carry out barium acetate by Na2O conversion, carry out preferential grinding of 20g, nitric-acid nature alumina binder 14g, and the 1500g of the pure water to 20g by BaO conversion, make powder T618g, powder U530g, powder V88g, and a sodium hydroxide into a slurry, and they were made to adhere to Catalyst BG, it dried and calcinated and the catalyst BGN1 which carried out the coat of 147 g/L to Catalyst BG was acquired. The amount of Pd support of this catalyst BGN1 was [3.18 g/L and the amount of Rh support of 12.0 g/L and the amount of Pt support] 3.88 g/L. The catalyst BGN1 was made into the structure shown in drawing 5 .

[0046] [Preparation of catalyst for NOx purification] powder T618g, and powder U530g, 20g and barium acetate by BaO conversion by Na2O conversion for powder V88g and a sodium hydroxide 20g, Carried out preferential grinding of the 1500g of the pure water to nitric-acid nature alumina binder 14g, considered as the slurry, and it was made to adhere to the nature monolith support of cordierite (400 cels / 6 mils, 1.3L), and dried and calcinated, and the catalyst N1 which carried out the coat of 147 g/L was acquired. The amount of Pd support of this catalyst N1 was [3.18 g/L and the amount of Rh support of 4.94 g/L and the amount of Pt support] 0.35 g/L. The catalyst N1 was made into monolayer structure. Moreover, magnesium acetate was used instead of the sodium hydroxide, the same actuation was repeated, and the catalyst N2 was acquired for the catalyst which supported 10 g/L as MgO and supported 10 g/L as BaO.

[0047] Carry out preferential grinding of 10g, nitric-acid nature alumina binder 9g, and the 1000g of the pure water by BaO conversion, make [preparation of three way component catalyst] powder T565g, powder F226g, and barium acetate into a slurry, and they were made to adhere to the nature monolith support of cordierite (900 cels / 2 mils, 1.3L), it dried and calcinated and the catalyst T0 which carried out the coat of 90 g/L was acquired. Furthermore, carried out preferential grinding of the 500g of the pure water to powder V128g and 200g of 0.8OCe0.2Zr2 powder, and nitric-acid nature alumina binder 12g, considered as the slurry, and it was made to adhere to a catalyst T0, and dried and calcinated, and the catalyst T1 of the two-layer structure which carried out the coat of 34 g/L to the catalyst T0 was acquired. 5.65 g/L and the amount of Rh support of the amount of Pd support of this catalyst T1 were 0.51 g/L.

[0048] The main catalyst components of each above-mentioned catalyst powder etc. were shown in the [catalyst specification] table 1, and the specification of the catalyst created by each above-mentioned catalyst preparation was shown in a table 2.

[0049]

[A table 1]

触媒粉末	担持貴金屬種		担持濃度 (%)	担持基材
	(一)			
A	Pd	10.0		CeO ₂
B	Pd	10.0		Zr _{0.1} Ce _{0.9} O ₂
C	Pd	10.0		Zr _{0.2} Ce _{0.8} O ₂
D	Pd	10.0		Zr _{0.5} Ce _{0.5} O ₂
E	Pd	10.0		Zr _{0.9} Ce _{0.1} O ₂
F	Pd	5.0		CeO ₂
G	Rh	6.0		Ca _{0.2} Zr _{0.8} O ₂
H	Rh	6.0		Mg _{0.1} Zr _{0.9} O ₂
I	Rh	6.0		Ba _{0.1} Zr _{0.9} O ₂
J	Rh	6.0		Sr _{0.2} Zr _{0.8} O ₂
K	Rh	6.0		Ca _{0.1} Mg _{0.1} Zr _{0.8} O ₂
L	Rh	6.0		Ca _{0.1} Ba _{0.05} Mg _{0.05} Zr _{0.8} O ₂
M	Rh	6.0		Ca _{0.01} Zr _{0.99} O ₂
N	Rh	6.0		Ca _{0.5} Zr _{0.5} O ₂
O	Pd	15.0		Al ₂ O ₃
P	Pd	15.0		Ce3%-Al ₂ O ₃
Q	Pd	15.0		Zr3%-Al ₂ O ₃
R	Pd	15.0		La3%-Al ₂ O ₃
S	Pd	15.0		Zr10%-Al ₂ O ₃
T	Pd	8.0		Al ₂ O ₃
U	Pt	6.0		Al ₂ O ₃
V	Rh	4.0		Al ₂ O ₃

[0050]

[A table 2]

触媒	触媒構造	貴金屬担持量(g/L)			(g/L) 7h加)		HC吸着材層	第一層	第二層	第三層
		Pd	Pt	Rh	(g/L) 7h加)	(g/L) 7h加)				
AG1	図3	7.06	—	3.53	—	—	β (Si/2AF=25)	A	G	—
AG2	図3	7.06	—	3.53	—	—	β (Si/2AF=15)	A	G	—
AG3	図3	7.06	—	3.53	—	—	β (Si/2AF=300)	A	G	—
AG4	図3	7.06	—	3.53	—	—	β (-25)+ZSM5(30)	A	G	—
AG5	図3	7.06	—	3.53	—	—	β (-25)+USY(=15)	A	G	—
AG6	図3	7.06	—	3.53	—	—	β (-25)+USY(=15)	A	G	—
AG7	図3	7.06	—	3.53	—	—	β (-25)	A	G	—
BG	図3	7.06	—	3.53	—	—	β (-25)	B	G	—
CG	図3	7.06	—	3.53	—	—	β (-25)	C	G	—
DG	図3	7.06	—	3.53	—	—	β (-25)	D	G	—
EG	図3	7.06	—	3.53	—	—	β (-25)	E	G	—
FG	図3	7.06	—	3.53	—	—	β (-25)	F	G	—
BAH	図3	14.12	—	3.53	—	—	β (-25)	B+A	H	—
BAI	図3	14.12	—	3.53	—	—	β (-25)	B+A	I	—
BAJ	図3	14.12	—	3.53	—	—	β (-25)	B+A	J	—
BAK	図3	14.12	—	3.53	—	—	β +ZSM5	B+A	K	—
BAL	図3	14.12	—	3.53	—	—	β +USY	B+A	L	—
BAM	図3	14.12	—	3.53	—	—	β +USY	B+A	M	—
BAN	図3	14.12	—	3.53	—	—	β +USY	B+A	N	—
OBAL	図4	21.18	—	3.53	—	—	β +USY	B+A	O	L
PBBK	図4	21.18	—	3.53	—	—	β +USY	B+A	P	2×B
QBCJ	図4	21.18	—	3.53	—	—	β +ZSM5	B+A	Q	B+C
RBDI	図4	21.18	—	3.53	—	—	β +USY	B+A	R	B+D
SBEH	図4	21.18	—	3.53	—	—	β +USY	B+A	S	B+E
OBFG	図4	21.18	—	3.53	—	—	β +USY	B+A	T	B+F
BGN1	図5	12.0	3.18	3.88	(Na ₂ O) ₂	(BaO) ₂₀	β	B	G	T+U+V
N1	第一層	4.94	3.18	0.35	(Na ₂ O) ₂	(BaO) ₂₀				
N2	第一層	4.94	3.18	0.35	(MgO) ₁₀	(BaO) ₁₀				
T1	第一層	5.85	—	0.51	—	(BaO) ₁₀				

[0051] The <performance evaluation of each catalyst> performance evaluation performed vehicles evaluation, and measured the discharge of each exhaust gas component when running in the FTP-75 mode (LA-4) which is a static test mode in North America. The exhaust gas purification structure of a system used for this performance evaluation is shown in drawing 6. This system consists of catalysts 1 and 2, an engine 10, a fuel injection equipment 11, O₂ sensor 12, and ECU13. On vehicles, the catalyst shown in a table 3 at the catalyst 1 by the side of an emission style on the street has been arranged, N1 which is the above-mentioned catalyst for NO_x purification, or N2 has been arranged for the catalyst 2 of the downstream, and it considered as examples 1-30 and the example 1 of a comparison. the above-mentioned system purified exhaust gas and the survival rate of HC, CO, and NO_x was investigated in the formula expressed with degree type ** survival rate = {1-(HC [in the exhaust gas of an NO_x purification catalyst outlet], CO, NO_x discharge)/(HC [in the exhaust gas of an engine out], CO, NO_x discharge)} x100(%) --** (HC in the above-mentioned exhaust gas, CO, and an NO_x discharge show the discharge when running the above-mentioned vehicles evaluation mode). Moreover, a table 3 is the value calculated using the transit portion immediately after the start in the case of running in the above-mentioned vehicles evaluation mode, NO_x of the portion specifically excluding after the start in the FTP-75 mode, and the transit portion by about 200 seconds, and the average concentration of each component of HC. Moreover, HC concentration was similarly calculated using average concentration. Non-burned HC

is discharged immediately after an engine start, and HC concentration of having removed the transit portion immediately after a start is because it becomes high and cannot evaluate correctly. In addition, the performance evaluation was performed on the conditions shown below.

[0052]

(Durable conditions)

Engine displacement 3000 cc Fuel The Nippon Oil dash gasoline (Pb=0 mg/usg, S= 30 ppm or less)

Catalyst inlet gas temperature 650 degrees C Durable time amount 50 hours [0053]

(Performance-evaluation conditions)

Catalyst capacity Catalyst 1: Catalyst of this invention 1.3L Catalyst 2:NOx purification catalyst 1.3L Evaluation vehicles Nissan Motor Co., Ltd. make Direct injection 1.8L engine [0054] The obtained result was shown in a table 3.

[0055]

[A table 3]

	搭載 位置		残存率 (%)		
	1 触媒	2 触媒	HC	CO	NOx
実施例1	AG1	N1	1.3	1.9	2.4
実施例2	AG2	N1	1.2	1.8	2.2
実施例3	AG3	N1	1.1	1.7	2.1
実施例4	AG4	N1	1.1	1.8	1.9
実施例5	AG5	N1	1.2	1.8	2.0
実施例6	AG6	N1	1.2	1.7	2.0
実施例7	AG7	N1	1.2	1.8	2.1
実施例8	BG	N1	1.2	1.7	1.9
実施例9	CG	N1	1.3	1.6	2.1
実施例10	DG	N1	1.3	1.6	2.2
実施例11	EG	N1	1.2	1.7	2.0
実施例12	FG	N1	1.2	1.8	2.1
実施例13	BAH	N1	1.1	1.9	1.9
実施例14	BAI	N1	1.1	1.8	1.9
実施例15	BAJ	N1	1.1	1.8	2.0
実施例16	BAK	N1	1.2	1.8	2.0
実施例17	BAL	N1	1.1	1.9	2.1
実施例18	BAM	N1	1.2	1.8	2.1
実施例19	BAN	N1	1.3	1.8	2.2
実施例20	OBAL	N1	1.4	2.0	2.2
実施例21	PBBK	N1	1.2	1.8	2.1
実施例22	QBCJ	N1	1.1	1.9	1.9
実施例23	RBDI	N1	1.1	1.8	1.9
実施例24	SBEH	N1	1.1	1.8	2.0
実施例25	OBFG	N1	1.2	1.8	2.0
実施例26	BGN1	N1	1.3	2.4	2.2
実施例27	AG1	N2	1.2	1.7	2.0
実施例28	BG1	N2	1.3	1.6	2.1
実施例29	BAH	N2	1.2	1.7	2.1
実施例30	OBFG	N2	1.1	1.8	2.0
比較例1	T1	N1	4.2	7.1	7.3

[0056]

[Effect of the Invention] As mentioned above, by according to this invention, performing specific HC reforming processing, CO steam-reforming processing, etc., generating H₂, and using these H₂ as an NO_x reducing agent, as explained Under a hyperoxia ambient atmosphere, it can be efficient, and NO_x can be purified by using H₂ as a

reducing agent, and HC in HC discharged by un-purifying, CO component, especially the low-temperature region after engine starting can be reduced remarkably, and, moreover, the high catalyst for exhaust gas purification of the improvement effect in fuel consumption can be offered.

[Translation done.]

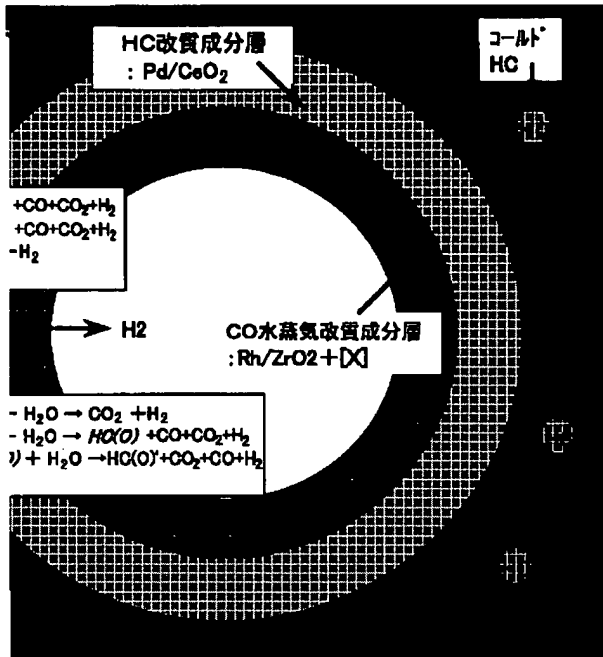
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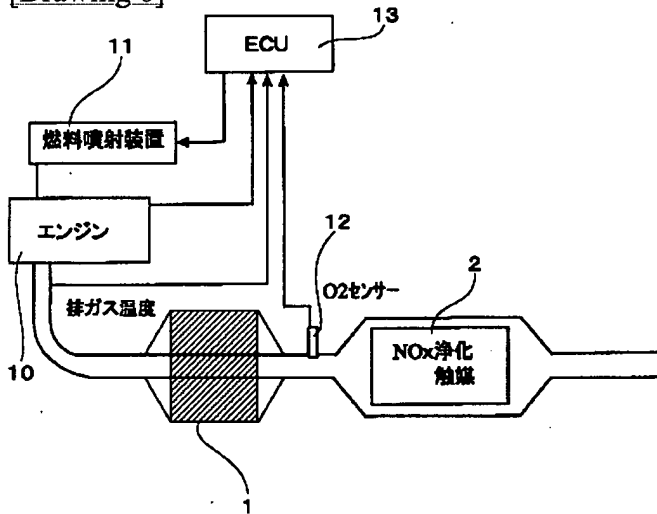
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DRAWINGS

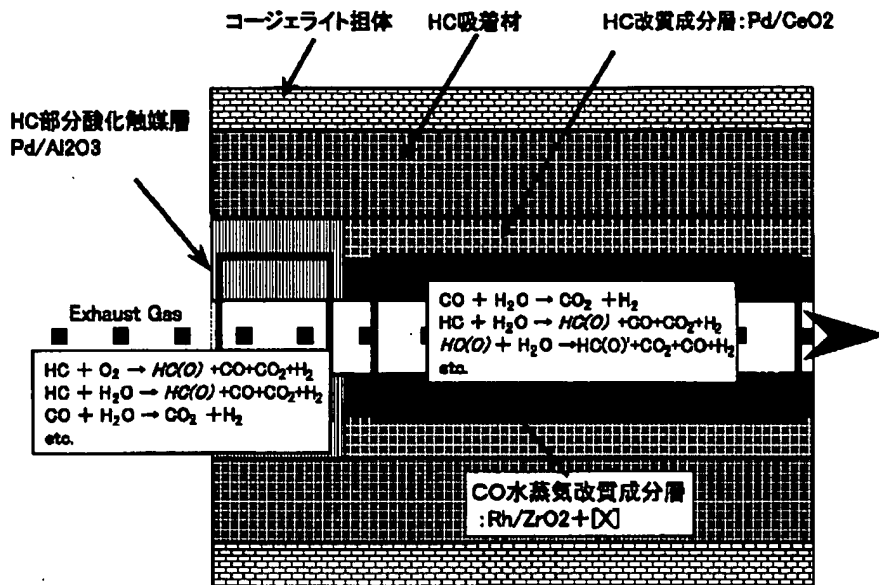
[Drawing 1]



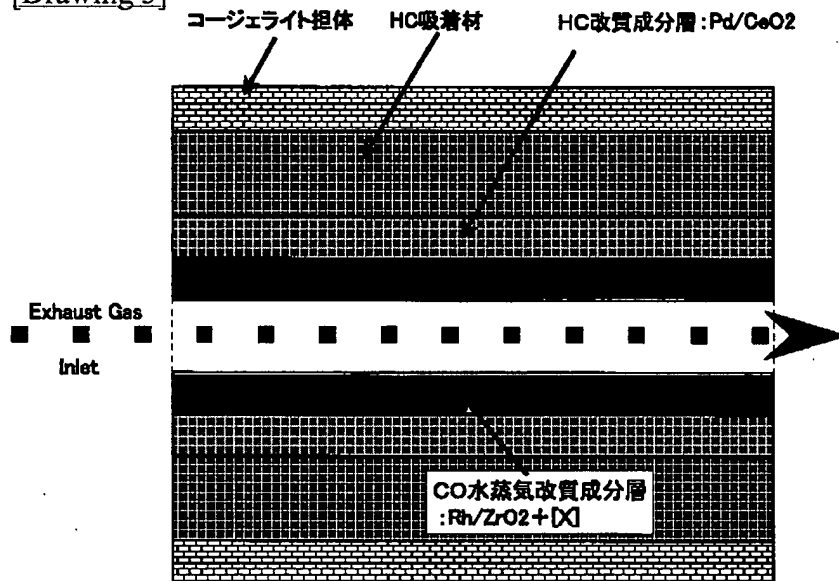
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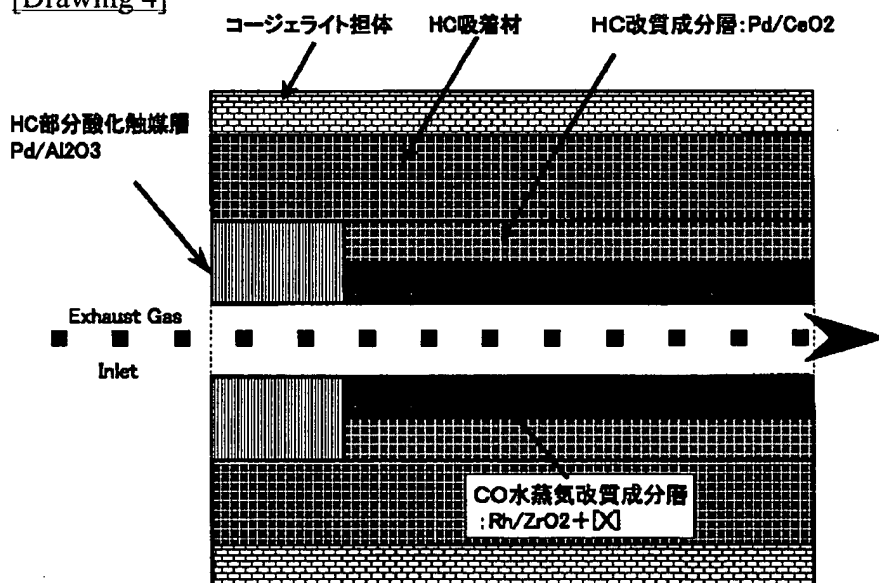
[Drawing 2]



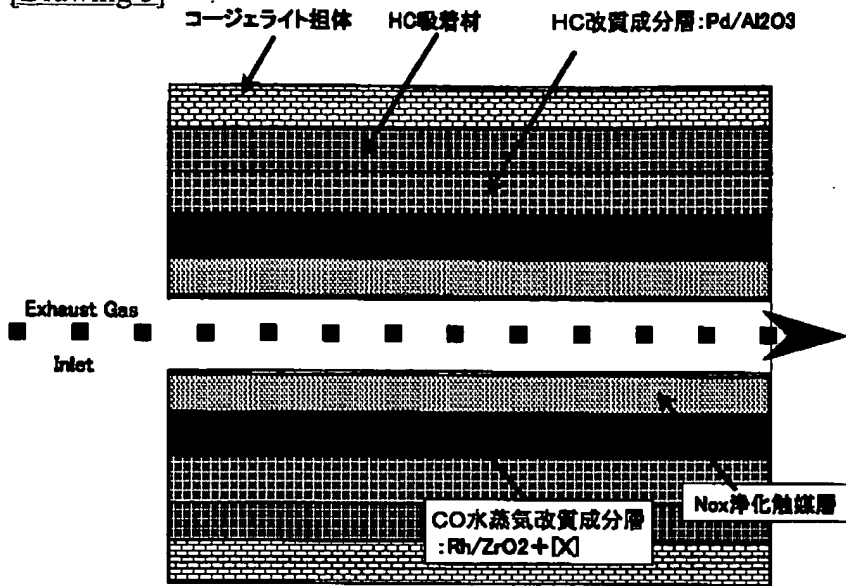
[Drawing 3]



[Drawing 4]



[Drawing 5]



[Translation done.]